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PUBLICATIONS

NBSIR 80-2108

Technical Activities 1980
Center for Materials Science

John B. Wachtman, Jr., Director
Darrell H. Reneker, Deputy Director

Center for Materials Science
National Measurement Laboratory
National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234

October 1980

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TECHNICAL ACTIVITIES 1980
CENTER FOR MATERIALS SCIENCE

John B. Wachtman, Jr., Director
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Center for Materials Science
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Washington, DC 20234

October 1980

Prepared for:
National Bureau of Standards
Department of Commerce
Washington, DC 20234

U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, *Secretary*

Jordan J. Baruch, *Assistant Secretary for Productivity, Technology, and Innovation*

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

ABSTRACT

The Center for Materials Science is part of the National Measurement Laboratory, one of the two principal laboratories comprising the National Bureau of Standards. The Center is organized in six Divisions, each having responsibility in different areas of materials science appropriate to the major classes of materials--metals, polymers, and ceramics and glass. These Divisions vary in their balance between theory and experiment, between direct standards work and research, and in their orientation toward industrial and Government needs and the needs of other components of the scientific and technical community. This volume summarizes the technical research activities and accomplishments of the six Divisions of the Center for Materials Science for fiscal year 1980.

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I. Introduction

The Center for Materials Science (CMS) was formed in 1978 as part of a general reorganization of the National Bureau of Standards. The Center is located within the National Measurement Laboratory (NML), one of the two principal laboratories comprising NBS. Figures 1, 2, and 3 give the organizational structure of the CMS, NML, and NBS, respectively. The CMS is one of the largest Centers at NBS. It has approximately 344 staff members; ∿ 68 percent are professionals, of which 61 percent hold Ph.D. degrees. The operating budget of the Center for FY80 amounted to ∿ $23 M.

The long-term goal of the Center for Materials Science is to support the private sector and other Government agencies in the most effective application and utilization of materials--metals, polymers, and inorganic materials. Center activities currently focus on those aspects of materials research involving processing science, structure/property science, and durability science. More specifically the Center

Develops and maintains the scientific competences and experimental facilities necessary to provide the Nation with a central basis for uniform physical measurements, measurement methodology, and measurement services necessary to define the properties and performance of materials and other essential areas in the materials science discipline.

Provides Government, industry, universities, and consumers with essential standards, measurement methods, data, concepts, and information concerning metals, polymers, and inorganic materials.

Characterizes the structure of materials, chemical reactions, and physical properties which will lead to the safest, most efficient uses of materials, improve materials technologies, and encourage recycling.

Obtains accurate experimental data on the behavior and properties of materials over time under service conditions to assure effective utilization of raw materials and manufactured materials.

Provides technical information in the form of reference data, materials measurement methods, and standards to materials processors, designers, and materials users to enable them to select cost effective combinations of materials, processes, designs, and service conditions.

The Center is organized in six Divisions, each having responsibilities in different areas of materials science. These Divisions vary in their balance between theory and experiment, between direct standards work and research, and in their orientation toward industrial and Government needs and the needs of other components of the scientific and technological community. The research activities of the Divisions are structured according to a task system; each task has specific goals, objectives, and milestones which support the overall goals of the Center. The following listing tabulates the tasks for each Division. Detailed descriptions of FY80 technical activities encompassed by the various tasks are given in the following sections.

Task Numbers, Titles, and Leaders

Center Office		
12101	Materials Measurement Services	J. B. Wachtman, Jr.
Chemical Stability and Corrosion Division		
12111	Corrosion and Chemical Stability of Materials in Service Environments	T. D. Coyle
12112	High Temperature Chemical Stability of Materials for Processing and Service	T. D. Coyle
Fracture and Deformation Division		
12121	Fracture Mechanisms and Analyses	R. P. Reed
12122	Durability of Ceramics and Composites	S. M. Wiederhorn
12123	Elastic-Plastic Fracture Mechanics	H. I. McHenry
Polymer Science and Standards Division		
12132	Polymer Standards for Control and Equity	L. E. Smith
12133	Predictive Models for Polymer Performance	B. M. Fanconi
12134	Chemical Durability of Plastics in Use	L. E. Smith
12135	Manufacture and Durability: Dental Medical Materials	J. M. Cassel
12136	Mechanical Durability of Plastics for Design and Use	B. M. Fanconi
12138	Migration and Durability of Plastics in Use	L. E. Smith
12139	Dielectric Plastics Design and Performance	M. G. Broadhurst
Metallurgy Division		
12142	Alloy Structure, Properties, and Standards for Quality Control	J. A. Simmons
51105	Synchrotron Radiation Research for Materials Science	M. Kuriyama
12143	Metallurgical Processing for Alloy Durability	J. R. Manning
12144	Alloy Durability for Wear Applications	A. W. Ruff
12145	Chemical Metallurgy for Durability	L. H. Bennett

Ceramics, Glass, and Solid State Science Division

12151	Structural Chemistry for Ceramic Processing and Durability	R. S. Roth
12153	Structural Methods for Processing Manufacture and Durability	S. Block
12154	Property, Structure, and Standards for Glass Processing and Manufacture	W. K. Haller
12155	Durability of Ceramics and Glass in Service Environments	H. P. R. Frederikse

Reactor Radiation Division

12161	Reactor Operation and Services	T. M. Raby
12162	Neutron Scattering Characterization of Materials for Advanced Technology	J. J. Rush
51102	Advanced Neutron Methods	J. M. Rowe
12163	Neutron Diffraction and Radiographic Methods for Materials Utility and Durability	J. J. Rush

OFFICE OF THE CENTER FOR MATERIALS SCIENCE

John B. Wachtman, Jr., Director
Darrell H. Reneker, Deputy Director
Samuel J. Schneider, Special Assistant for Programs
Bruce W. Steiner, Special Assistant for Planning and Programming
John D. McKinley, Special Assistant for Program Planning and Initiation
Melvin Linzer, Leader, Signal Processing and Imaging Group
Robb M. Thomson, Center Scientist
John W. Cahn, Center Scientist
Jacob Mazur, Center Scientist
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Ellen T. King, Supervisory Editorial Assistant
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M. Jocelyn Castle, Senior Administrative Officer
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Marian L. Slusser, Administrative Officer
Ruth A. Schmeit, Administrative Assistant
Diane Shields, Administrative Assistant
Sara M. Thomas, Administrative Assistant
Patricia F. Hernandez, Administrative Aide

The Center Office has the responsibility for providing the technical and administrative framework for the planning and operation of the technical programs carried out by the six Divisions and the Center Office scientists. Efforts this past year have focused on the development, strengthening, and implementation of programs and plans of the Center. Although the majority of the activities of the Center Office are reflected through accomplishments of the Divisions, several of particular interest merit mention here:

A Congressionally-mandated study of the costs of fracture to the U.S. economy is being initiated by the Center. This will be implemented under Center Office oversight beginning in FY81.

The Center's formal long-range (five-year) plan has been rewritten and up-dated to reflect new competence building thrusts, new programmatic plans in innovative high performance materials, recent shifts in task emphasis, and to review relevance of Center activities to critical national issues in materials recently identified by the National Materials Advisory Board (NMAB) of the National Academy of Science (NAS).

Center units have participated as organizer, sponsor, or host for the following technical meetings:

Fourth Annual Conference on Materials for Coal Conversion, October 9-11, 1979

Workshop on Materials for Superconducting Magnets, October 16-18, 1979

Conference on Implant Retrieval: Material and Biological Analysis, May 1-2, 1980

Conference on Basic Optical Properties of Materials, May 5-7, 1980

International Standards Organization Technical Committee 156 on Corrosion of Metals, June 1-16, 1980

Second International Symposium on Ultrasonic Materials Characterization, June 4-6, 1980

Inter-American Conference on Materials Technology, ASME, August 12-16, 1980

Measurement Services
Task 12101

Although most of the program planning and laboratory activity in the Center takes place in the six Divisions, a single task, Measurement Services, in the Center Office takes a general view of American materials science. This task assures adequate attention to major new challenges and opportunities, particularly those that may affect two or more Divisions. This activity also provides a window on policy studies in the Executive and Legislative Branches. At the same time, through this activity, the Center provides senior consultation to other agencies, to other NBS Centers, and to CMS Divisions.

Signal Processing and Imaging
Subtask 1 of Task 12101

M. Linzer, S. I. Parks, S. J. Norton, and J. A. Abbott[1]

[1]Postdoctoral Research Associate

In the past year, emphasis was placed on various aspects of ultrasonic imaging and computerized tomography. A theoretical and experimental analysis of texture in ultrasonic imaging was carried out. Studies of cutting techniques for transducer arrays and tomographic image reconstruction from limited projections were completed. A collaborative effort with the National Institutes of Health (NIH) Clinical Center showed that an NBS-developed digital processing device was capable of diagnosing diffuse liver pathology (e.g., Gaucher's disease). Exact solutions were obtained for the first time for three-dimensional reflectivity imaging using broad bandwidth pulses. Inversion formulas were derived for three transmit-receive apertures--plane, cylindrical, and spherical. Substantial progress was made in developing perturbation and iterative correction schemes for velocity tomography. The theoretical and computer simulation phase of this activity is expected to be completed during the first half of the next fiscal year and experimental demonstration of the techniques in the second half.

Two papers were published, three accepted for publication, and a book, Ultrasonic Materials Characterization, was edited.

Fracture Theory
Subtask 2 of Task 12101

R. M. Thomson

A rigorous statistical mechanical theory of reaction rates at the tip of a fracture crack has been developed. This work puts the quasi-chemical approaches developed earlier on an adequate theoretical basis, and predicts new phenomena associated with bridging reactions at the crack tip which are yet to be observed. This paper was published during the year.

A second paper co-authored with Fuller applied results of the first paper to one-dimensional models, and developed laws for slow crack growth velocities as a function of applied stress. This paper was published during the year.

A third paper co-authored with Lawn and Fuller developed a fundamental theorem on the one-dimensional model of fracture which showed that one could break down the effects of chemical reaction at a crack tip into three separable physical effects: a) the chemical reaction at the tip molecule; b) elastic response of the remainder of the crystal; and c) the change in potential energy of external force systems. This theorem should be important in developing detailed ideas about crack tip chemistry, because of the absence of cross terms between the linear response of the lattice, and the response of the nonlinear reacting molecule at the tip. This paper is in press.

A fourth paper was co-authored with Fuller and Wiederhorn and delivered at a limited attendance international conference by Wiederhorn in Cambridge. The paper reviewed NBS theoretical ideas and experimental results in brittle fracture. The new result was a demonstration of how to generalize the concept of activation volume to crack growth laws.

A fifth paper now being prepared has reopened the theory of fracture in 2D and 3D discrete lattices. A new formulation has been developed in terms of lattice Greens functions. It is shown that all lattice theories must yield a finite lattice trapping--a controversial point of rigor until now. Asymptotic Greens functions were developed which vastly improve the ease and speed of discrete lattice calculations. Methods were developed for calculating activation energies and activation volumes for a variety of force laws. Methods were developed for handling general nonlinear force laws at the crack tip which were analytic and do not require numerical computer solution. And finally, the theorem that the overall response of a material can be broken into three separate parts (crack tip nonlinear atomic pair, linear lattice, and external force) is shown to be a completely general result for two and three dimensions as well as one.

New results have been obtained, but not yet in the write-up stage which a) show that a sharp fracture always has a $1/\sqrt{r}$ stress singularity at its tip because of limited screening due to dislocations, and b) developed rigorous solutions of idealized fracture modes which confirm an earlier approximate result which has become controversial regarding how the critical stress to fracture should depend upon the surface free energy. These results should lead to predictions of actual fracture criterion laws for brittle materials, ultimately.

Theoretical Materials Stability
Subtask 3 of Task 12101

John W. Cahn

This work addressed fundamental factors in the stability of materials. It is carried on with a wide variety of colleagues. This past year we have worked with colleagues in Montpellier, in Cambridge (Massachusetts), and in Malibu. The activity can be divided into two general areas, interface activity and bulk stability.

In addressing interface activity, they have shown first that in any two-phase mixture of fluids near the critical point, one of the phases will wet a third phase so that contact with the other phase is excluded. The surface layer of the wetting phase continues to exist past the onset of instability in the bulk phase. This perfect wetting terminates in a first-order transition which has been found and is being studied. For solids, a satisfactory microscopic theory for antiphase domain wall, motion in ordered structures has been demonstrated. The velocity of motion is predicted to be proportional to mean curvature, but independent of surface-free energy, in contrast to the unsatisfactory predictions of previous models. The behavior of FeAl and Cu_3Au alloys has been demonstrated to be consistent with that predicted.

For the growth of monotectic solid composites from solution, theoretical factors have been re-examined. There are indications that phase growth may be determined by the velocity necessary to overcome disjoining pressure, which will be small. Critical experiments have verified the analysis: variation in pressure and ternary additions. Perfect wetting should occur close to the critical temperature.

Equilibrium antiphase and interphase boundaries in the CuAu system have been examined. Near the congruent point antiphase boundaries undergo a second order surface phase transition to an interfacial layer resembling inhomogeneous CuAu. One of the antiphase boundaries is predicted to be perfectly wet by the disordered phase at the disordering temperature.

A two-dimensional lattice-gas model of a grain boundary has been investigated and shown to exhibit a phase transition that can be described as surface melting.

The role of higher order (non-pairwise) energies in FCC alloys has been examined and found to lead to a prediction of either symmetric or asymmetric versions of Cu-Au phase diagrams.

General conditions have also been established for multiphase equilibrium of anisotropically stressed solids in contact with fluids. The equilibrium obtained is sensitive both to the presence of vacancies and the nature of the phase contact. Equilibria at coherent boundaries are insensitive to the existence of vacancies, while vacancies do govern the equilibrium of incoherent phases.

Finally, reports that low temperature diffusion can cause grain boundaries to migrate and thereby provide a mechanism of greatly enhanced (by factors in excess of 10^9) diffusion have been confirmed and investigated in greater detail. The effect exists for at least six different metallic systems and for symmetric as well as unsymmetric boundaries.

<u>Processes Involving Conformational Changes in Polymers</u>
Subtask 4 of Task 12101

Darrell H. Reneker, J. Mazur

The infrared spectrum of polyethylene in which five percent of the carbon atoms are doubly deuterated contains bands which are attributed to trans-trans and trans-gauche dihedral angle sequences. These bands were used to analyze conformational disorder in crystalline polyethylene. Experimental results show that trans-gauche sequences occur in crystalline polyethylene and that the number of such sequences increases in the temperature range between 60° and 120 °C.

A defect in a polyethylene crystal known as a point dislocation or twist dispiration loop, which transports a chain along its axis through a crystal by a process appropriately called reptation, involves several trans-gauche sequences. The thermal generation and subsequent motion of such defects can account for a variety of experimentaly observed phenomena in polyethylene. The motion of the defect is being modeled mathematically at the level of conformational changes within the molecule and also by considering the defect as a point diffusing along a straight polymer chain segment bounded by two folds. The defect motion is considered to be driven both by fluctuating forces derived from thermal motions and by microscale forces derived from macroscopic strain. The theoretical analysis uses data from infrared and nuclear magnetic resonance spectroscopy to characterize the defects. The resulting model for dynamics of defect motion connects data from thermal annealing, dielectric relaxation, and mechanical relaxation experiments and thereby leads to improved understanding of the useful macroscopic properties of polymers.

The transport of polyethylene in the melt by a reptation process is being investigated. The self diffusion coefficient or molten polyethylene measured with a magnetic field gradient nuclear magnetic resonance method is being compared with diffusion coefficients measured by observing the changes in concentration of perdeuterated molecules near a boundary between polyethylene and polyethylene containing perdeutero-polyethylene as a function of time. This work extends the investigation of molecular transport by reptation into the melt.

Energy minimization calculations are being used to investigate the effects of fold geometry and temperature on the overall energy of a single crystal. The results of these calculations are being correlated with observations of changes in crystal morphology which occur with increasing crystallization temperature.

The above work is being done in cooperation with collaborators in the Polymer Science and Standards Division, the University of California in Berkeley, and the Josef Stefan Institute in Ljubljana, Yugoslavia.

Other Activities in the Office of the Center for Materials Science

Invited Talks

Polymer Morphology and Chain Transport Mechanism
Boris Kidric Institute, Belgrade, Yugoslavia
D. H. Reneker
September 1979

Properties of Polymers Including Chain Transport and Piesoelectric Effects
Josef Stefan Institute, Ljubljana, Yugoslavia
D. H. Reneker
September 1979

Role of Defects in Transport of Chains in Polymer Crystals
Northwestern University, Evanstan, Illinois
D. H. Reneker
April 1980

Colloquium, American Ceramic Society
Physics Department, Rutgers University, New Brunswick, New Jersey
R. M. Thomson
April 1980

Trends in Materials Science in the 80's and Some Associated Information Service Needs
Metals/Materials Division, Special Libraries Association
Washington, D.C.
John B. Wachtman, Jr.
June 1980

Mechanical Properties and Failure Avoidance
Committee on Capital Construction
Beijing, Peoples Republic of China
John B. Wachtman, Jr.
June 1980

Erosion of Ceramics
Committee on Capital Construction
Beijing, Peoples Republic of China
John B. Wachtman, Jr.
June 1980

The Program of the Center for Materials Science, National Bureau of Standards
Committee on Capital Construction
Beijing, Peoples Republic of China
John B. Wachtman, Jr.
June 1980

Mechanical Properties and Failure Avoidance
Shanghai, Peoples Republic of China
John B. Wachtman, Jr.
June 1980

Erosion of Ceramics
Shanghai, Peoples Republic of China
John B. Wachtman, Jr.
June 1980

Research on Ceramics in the Peoples Republic of China--A Trip Report
National Bureau of Standards
John B. Wachtman, Jr.
July 1980

Measurement Science and Technology at the National Bureau of Standards
Engineering Foundation Conference on National Materials Policy
New England College, Henniker, New Hampshire
John B. Wachtman, Jr.
July 1980

Spectroscopic Investigations of Conformational Irregularities in Crystalline Polymers
Polymers Department, Weizmann Institute of Science
Rehobot, Israel
J. Mazur
July 1980

Spectroscopic Investigations of Conformational Irregularities in Crystalline Polymers
Faculty of Chemistry, Israel Institute of Technology
Haifa, Israel
J. Mazur
August 1980

Assessment of MHD Technology
National Science Foundation Workshop
Washington, D.C.
S. J. Schneider
September 1980

Performance and Durability of Materials
Johns Hopkins University, Baltimore, Maryland
John B. Wachtman, Jr.
September 1980

Performance and Durability of Materials
Pennsylvania State University, State College, Pennsylvania
John B. Wachtman, Jr.
October 1980

Technical and Professional Committees and Leadership

Federation of Materials Societies

Committee on Materials Durability and Conservation
J. B. Wachtman, Jr., Chairman

Advisory Committee to Materials Research Laboratory, Pennsylvania State University
J. B. Wachtman, Jr., Member

Corporation Visiting Committee, Department of Materials Science and Engineering, Massachusetts Institute of Technology
J. B. Wachtman, Jr., Member

American Physical Society

J. B. Wachtman, Jr., Fellow
R. M. Thomson, Fellow
J. W. Cahn, Member

Committee on Applications of Physics
J. B. Wachtman, Jr., Member

Division of High Polymer Physics
D. H. Reneker, Program Chairman

Editorial Committee, Annual Review of Materials Science
J. B. Wachtman, Jr., Member

Mining/Metallurgy/Ceramics/Materials Engineering Peer Committee National Academy of Engineering
J. B. Wachtman, Jr., Member

Materials Science and Technology Committee
J. B. Wachtman, Jr., Member

Committee on Materials (COMAT)
J. B. Wachtman, Jr., Alternate Member

American Ceramic Society

J. B. Wachtman, Jr., Member
S. J. Schneider, Member
J. W. Cahn, Member
R. M. Thomson, Member

Executive Committee
J. B. Wachtman, Jr., Member

Rules Committee
J. B. Wachtman, Jr., Member

Refractories Division
S. J. Schneider, Editorial Chairman

Executive Committee
S. J. Schneider, Member

American Society for Testing and Materials

S. J. Schneider, Member
J. B. Wachtman, Jr., Member
R. M. Thomson, Member

C8 Refractories Committee
S. J. Schneider, Member

E20 Temperature Committee
S. J. Schneider, Member

Award of Merit Committee (National)
S. J. Schneider, Member

American Chemical Society

J. B. Wachtman, Jr., Member
J. D. McKinley, Member

US-USSR Cooperative Program on MHD

Steering Committee
S. J. Schneider, Member

Interamerican Conferences on Materials Technology

Executive Committee
S. J. Schneider, Member

IUPAC Conferences on Refractories for Energy Applications

Planning and Program Committees
S. J. Schneider, Member

Committee on Dynamic Compaction of Metal and Ceramic Powders

J. D. McKinley, Liaison Representative, NBS

Solid State Sciences Committee, National Research Council

Committee on Applied Physics
R. M. Thomson, Member

Plastics Institute of America

Research Committee
D. H. Reneker, Member

National Archives and Records Service

Advisory Committee on Preservation
D. H. Reneker, Member

Polymer Science and Engineering

Board of Editors
D. H. Reneker, Member

CRC Critical Reviews in Solid State Physics

Board of Editors
D. H. Reneker, Member

IUPAC 79 "Macromaining"
D. H. Reneker, Session Chairman

The Optical Society of America

Washington Area Drive for National Optics Center Fund
B. W. Steiner, Chairman

Technical Council
B. W. Steiner, Chairman

Executive Committee
B. W. Steiner, Member

Liaison with Society for Photo Optical Instrumentation Engineers
B. W. Steiner

American Institute of Metallurgical Engineers

Heat Treating Committee
J. W. Cahn, Member

Solidification Committee
R. M. Thomson, Member
J. W. Cahn, Member

National Academy of Sciences
J. W. Cahn, Member

American Academy of Arts and Sciences
J. W. Cahn, Fellow
R. M. Thomson, Member

American Society for Metals
R. M. Thomson, Member

Thermodynamics Committee
J. W. Cahn, Member

Archeological and History Committee
J. W. Cahn, Member

Publications

Further Development and Clinical Evaluation of the Expanding-Aperture Annular Array System
S. I. Parks, M. Linzer, and T. H. Shawker
Ultrasonic Imaging, 1, 378-383 (1979)

Raman Spectra of n-alkanes. I. Raman Intensities of Longitudinal Acoustic Modes
J. Mazur and B. Fanconi
J. Chem. Phys., 71, 5069 (1979)

Development of Tailored Materials and Processes
John B. Wachtman, Jr., and Bruce W. Steiner
Materials Eng., 91, 48 (1980)

Amplitude Analysis of Pancreatic B-Scans: A Clinical Evaluation of Cystic Fibrosis
T. H. Shawker, S. I. Parks, M. Linzer, B. Jones, L. A. Lester, and V. S. Hubbard
Ultrasonic Imaging, 2, 55-66 (1980)

Materials for Open Cycle MHD Generators
S. J. Schneider, H. P. R. Frederikse, T. Negas, and G. Rudins
Chapter 3, Current Topics in Materials Sciences, Vol. 4, E. Kaldis, North Holland Publishing Co. (1980)

Theory of Chemically Assisted Fracture I. General Reacton Rate Theory and Thermodynamics
R. M. Thomson
J. Matls. Sci., 15, 1014 (1980)

Theory of Chemically Assisted Fracture II. Atomic Models of Crack Growth
E. R. Fuller, Jr., and R. M. Thomson
J. Matls. Sci., 15, 1027 (1980)

Atomic Modeling of Chemical Interactions at Crack Tips
R. M. Thomson, B. R. Lawn, and E. R. Fuller, Jr.
Acta Met (in press)

Tomographic Image Reconstruction from Limited Projects Using Iterative Revisions in Image and Transform Spaces
T. Sato, S. J. Norton, M. Linzer, O. Ieda, and M. Hirama
Appl. Optics (accepted for publication)

Reflectivity Imaging in Three Dimensions: Exact Solutions for Plane, Cylindrical, and Spherical Apertures
S. J. Norton and M. Linzer
IEEE Trans. Biomed. Eng. (accepted for publication)

Optical Interferometric Visualization and Computerized Reconstruction of Ultrasonic Fields
F. P. Higgins, S. J. Norton, and M. Linzer
J. Acous. Soc. Amer. (to be published)

Micro Mechanisms of Crack Growth in Ceramics and Glass in Corrosive Environments
R. M. Thomson, S. M. Wiederhorn, and E. R. Fuller, Jr.
Proc. International Conference on Fundamentals of Fracture, Cambridge, England (to be published)

Measurement Science and Technology at the National Bureau of Standards, Center for Materials Science
J. B. Wachtman, Jr., and J. D. McKinley
Proc. VI Henniker Conference on National Materials Policy (to be published)

Sponsored Conferences

Fourth Annual Conference on Materials for Coal Conversion and Utilization
National Bureau of Standards
October 1979

Fifth International Symposium on Ultrasonic Imaging and Tissue Characterization
National Bureau of Standards
June 1980

Second International Symposium on Ultrasonic Materials Characterization
National Bureau of Standards
June 1980

Fracture Workshop
DARPA Materials Research Council
La Jolla, California
July 1980

Metals Processing, ASME
San Francisco, California
August 1980

Incentives and Disincentives for Conservation of Materials and Effective Utilization of Materials Through Product Design
Session at VI Henniker Conference on National Materials Policy
New England College, Henniker, New Hampshire
August 1980

Fifth Annual Conference on Materials for Coal Conversion and Utilization
National Bureau of Standards
October 1980

NATO Fracture Conference
Spril 1981

Mechanical Properties Symposium
American Physical Society
1981

Topical Conference on Fundamental Physics of Mechanical Behavior for American Physical Society
1981

Fracture Fundamentals Conference
1982

Books

Ultrasonic Materials Characterization
H. Berger and M. Linzer, Eds.
American Society for Nondestructive Testing

Materials Aspects of World Energy Needs
J. B. Wachtman, Jr., Ed.
National Research Council

Issues and Engineering Education
National Academy of Engineering
J. B. Wachtman, Jr., Ed.

Special Reports

Evaluation of Ultrasound Echo Amplitude Measurements for Assessment of Bond Integrity in Zirconium Alloy Samples
M. Linzer, J. G. Abbott, and S. I. Parks
Report on Westinghouse Contract No. EY-76-C-11-0014

An Assessment of Open Cycle Magnetohydrodynamics (MHD) Technology
S. J. Schneider, T. Negas, W. R. Hosler, and J. D. McKinley
August 1980

CHEMICAL STABILITY AND CORROSION DIVISION (561)

Thomas D. Coyle, Chief
L. L. Ware, Administrative Aide
M. L. Seebode, Clerk Typist
M. E. Lukens, Clerk Typist
M. S. O'Connor, Student Aide
R. M. Gregory, Clerk Typist

The Chemical Stability and Corrosion Division provides a focus, within the NBS Center for Materials Science, for research and measurement activities related to the chemical stability and reactivity of materials in their service environments. The Division carries out field and laboratory research to assess the resistance of materials to chemical and biological degradation under service conditions. It identifies and characterizes the mechanisms underlying corrosion, corrosion inhibition, and molecular level chemical transformations critical to materials stability and processing and to the environmental impact of materials use. As required, it develops measurement methods for quantitative characterization of degradation processes, test methods to predict in-service durability, and appropriate standards.

The Division's accomplishments during FY80 are described in the following pages. The program is described here in terms of three tasks. One of these emphasizes metallic corrosion and the chemical stability of materials in ambient service environments. A second focuses on chemical processes affecting materials durability and processing at high temperatures. A third area of activity includes work on the chemical properties and performance of lubricants in support of the NBS Recycled Oil Program. Research is discussed under subtasks of these three tasks which comprise groups of individual but integrated research projects.

CORROSION AND CHEMICAL STABILITY OF MATERIALS IN SERVICE ENVIRONMENTS
Task 12111

The objective of the work carried out under this task is to provide data, measurement methodology, test methods, and standards required in processing, design, manufacture, and use; to enhance chemical durability of materials (including corrosion resistance); and to reduce adverse impacts of chemical and biodegradation of materials on health, safety, and the environment.

The technical activities fall into two subtask areas. One subtask emphasizes metallic corrosion and protective coatings. The other subtask focuses on measurement methodology and mechanistic understanding of chemical and biodegradation processes affecting several classes of materials.

Corrosion and Electrodeposition
Subtask 1 of Task 12111

J. Kruger, N. K. Adams, U. Bertocci, W. E. Crummer, C. F. Derr, E. Escalante, J. L. Fink, W. F. Gerhold, S. Ito, C. E. Johnson, D. R. Kelly, D. S. Lashmore, J. S. Mullen, F. Ogburn, E. N. Pugh, J. J. Ritter, M. J. Rodriguez, B. T. Sanderson, J. Smit, J. P. Young

Technical activity in this area is aimed at providing a scientific base, data, measurement methodology, test methods, and standards to advance corrosion prevention and coating technologies. It carries out this objective by working on projects that range from test method development through field and laboratory studies of corrosion resistance of materials, to more basic investigations of corrosion mechanisms, and coatings science.

Corrosion Science, Measurement, and Test Methods: This area seeks to develop, improve, and evaluate test methods which will measure pitting, crevice and stress corrosion, hydrogen embrittlement, gaseous oxidation, underground, marine, and atmospheric corrosion in order to provide industry and Government with improved test methods. To accomplish these objectives, the approach is to apply the newest techniques provided by electrochemistry, metallurgy, surface physics, and chemistry to a study of corrosion processes and to eventually develop from these studies simpler techniques that can be applied by testing laboratories.

Significant technical activities during FY80 in this area have been the following:

(1) The feasibility of deriving useful information from a new technique that can make simultaneous ellipsometric and electrochemical measurements on iron protected by an organic coating has been demonstrated. This work was partially supported by the Office of Naval Research and seeks to develop a better understanding of corrosion processes occuring under paints in order to provide a basis for the development of coatings

with enhanced corrosion resistance. Results obtained from polished iron specimens protected by a 10-30 μm coating of cellulose nitrate and immersed in dilute NaCl solution indicate that active corrosion is a highly localized process. A major portion of the remaining surface is subjected to a predominately alkaline environment as a consequence of the cathodic reduction of O_2. The latter regions, when observed ellipsometrically show both surface roughening and a substantial thickening of the existing substrate oxide film. This behavior of iron in highly alkaline media has been experimentally verified by ellipsometric studies of iron in saturated NaOH.

The presence of an inhibitor ion such as CrO_4^{-2} appears to attenuate both surface roughening and oxide film thickening, (see figure 1).

The topographical changes which occur on the substrate surface under the coating (i.e., surface roughening and oxide film thickening) are believed to contribute to the early stages of coating failure in that they promote loss of adhesion.

(2) Further progress has been made in the development of electrochemical noise measurements and their application to the study of corrosion processes. This work, partially supported by the NBS Office of Nondestructive Evaluation, promises to give new insights into corrosion mechanisms as well as provide the basis for new test methods. Improvements in our ability to interpret corrosion noise measurements were achieved during the past year when it was shown that by calculating the cross-power spectrum between the input (the electrode potential) and the output (the cell current) of an electrochemical system under potentiostatic conditions, it was possible to identify which part of the cell current is the response to the input voltage and which part is caused by random fluctuations of the parameters characterizing the electrode. The noise introduced by the amplifiers can thus be measured separately and then subtracted from the signal. Using this new refinement of the technique it could be shown that on aluminum the degree of random fluctuations below the pitting potential is so low that the picture of the protective film as being in a state of dynamic equilibrium with continuous breakdown and repair does not seem to be supported by the experimental evidence.

A new application of the electrochemical noise measurements made during the past year involved an examination of the dynamic processes occurring on the corroding surface of an amorphous alloy, which is supposed to have superior corrosion resistance. Figure 2 shows clearly the remarkable difference in the noise spectra of the amorphous material and the same alloy after being crystallized. The latter is seen to have a much greater tendency to localized attack, no doubt because of structural inhomogenity of the passive film. Moreover, the noise measurements have revealed that the superior resistance to breakdown of the passive film in the amorphous alloy is not a result of the static properties of this film because the overall current densities observed did not differ greatly when comparing the crystallized and amorphous alloys. Rather, the greater resistance to breakdown of the amorphous alloy lay in the ability of its more homogeneous film to inhibit the dynamic processes

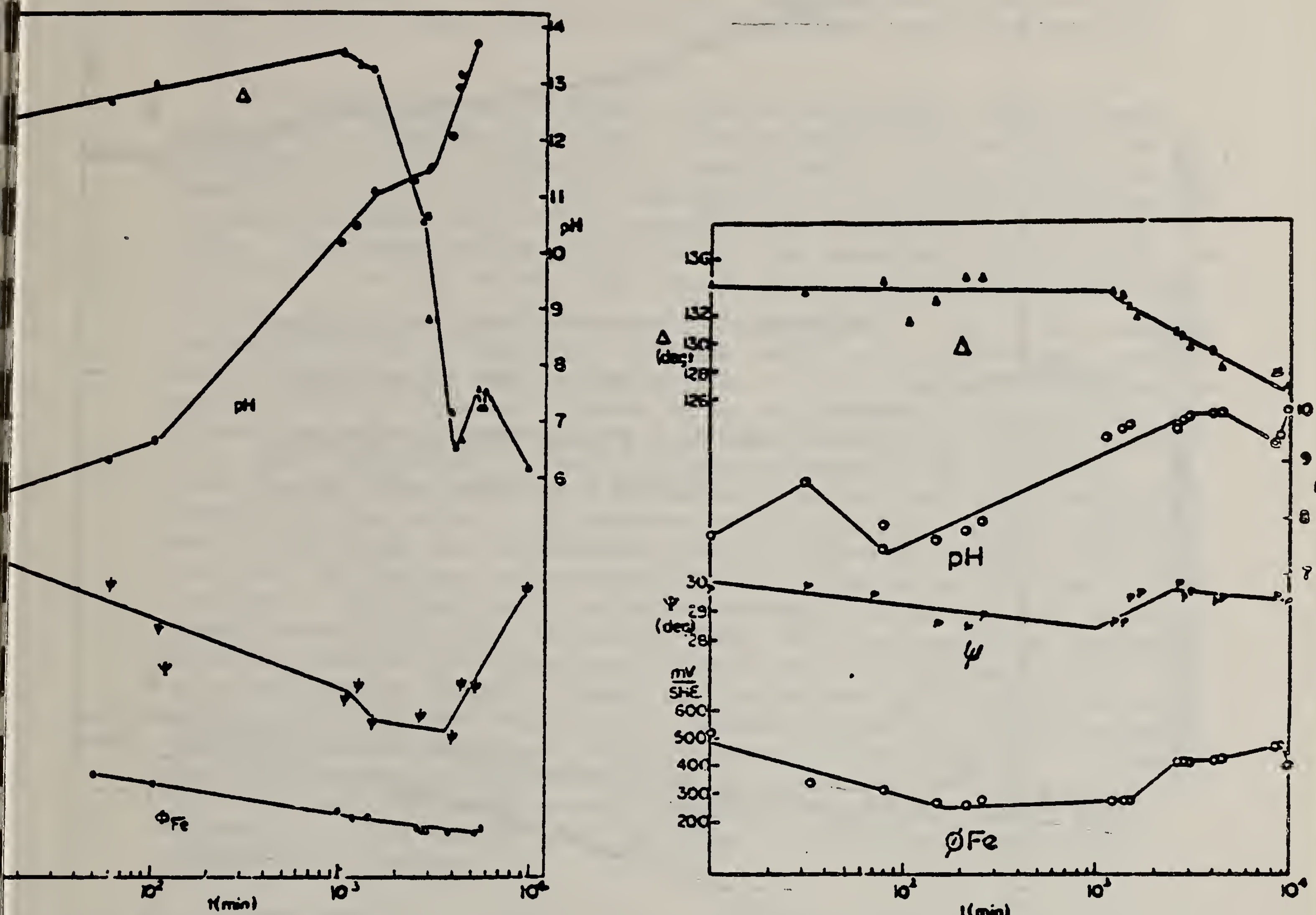

Figure 1. The changes with time of the optical parameters Δ and ψ, which indicate metal roughening and oxide film growth, potential (ϕFe) and pH for (a) iron covered with collodian and immersed in 0.05 N NaCl, and (b) iron with collodian and CrO_4^{-2} islands in 0.05 N NaCl.

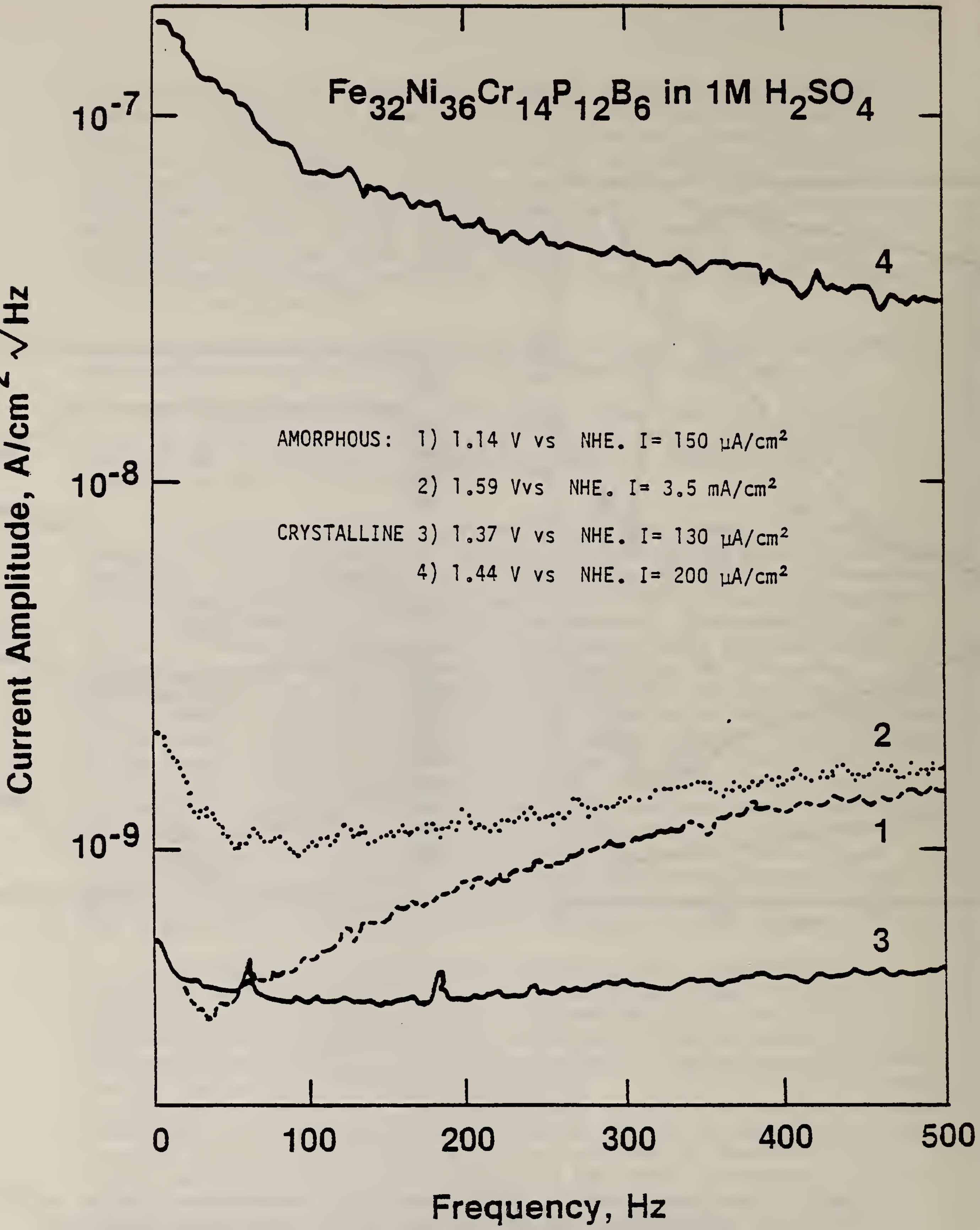

Figure 2. Noise current spectra for amorphous and crystalline $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ in 1 M H_2SO_4. Curves 1 and 3 are at potentials where pitting should not occur; curves 2 and 4 are above or at potentials where pitting should be possible.

(probably repeated breakdown-repair events) that result in electrochemical noise. These results with the amorphous and recrystallized alloys bolster the suggestion that the breakdown mechanism involves a dynamic fluctuating set of events (for example, damaging species penetration) rather than a steady deterioration of the properties of the passive film.

(3) A new program in stress corrosion and hydrogen embrittlement was started during the past year. A major aim of this new effort is to evaluate and develop methods for stress-corrosion testing. Both the double-torsion and slow-strain-rate methods are currently being used to evaluate the stress-corrosion susceptibility of high-purity Al-Zn-Mg alloy. The former method yields data on the dependence of the crack velocity, V, on the stress intensity, K, and on $K_I$scc, the stress intensity at which crack growth becomes negligibly small; the latter measures susceptibility more indirectly from the reductions in strain to fracture and maximum stress. Work on the effects of heat treatment on the performance of the Al alloy was started using both methods to compare the respective rankings. During the year, work carried out in conjunction with the Univeristy of Illinois at Urbana-Champaign has employed a load-pulsing technique which provides a convenient and simple method of determining the velocity of stress-corrosion cracks. In this technique, small load pulses are superimposed onto an otherwise constant tensile load and, in the case of transgranular stress-corrosion cracking of austenitic stainless steels and alpha-brasses, the pulses were found to produce markings on the fracture surfaces which delineate the instantaneous positions of the crack front. The crack velocity can then be obtained from the spacing between the crack-front markings, Δx, measured with the SEM, and the time interval between pulses, Δt. Tests to date indicate that the velocity is not influenced by the pulsing. The tests are being extended to the Al-Zn-Mg alloy to compare the plateau velocity, i.e., the velocity in the stress-independent region of the V-K curve, determined by the load-pulsing technique with that obtained in the double-torsion method.

Interpretation of the results of stress-corrosion tests requires a knowledge of the mechanisms of these critically important fracture processes, and consequently efforts were also directed to this area. The load-pulsing method has recently been used to address the controversial question of whether the propagation of transgranular stress-corrosion cracks is a continuous (dissolution) or discontinuous (mechanical) process. In tests on a Type 310 austenitic stainless steel, Δx, was found to decrease progressively with decreasing Δt until a limiting value of $\sim$ 0.5 μm was attained (for $\Delta t \sim$ 15 s). The limiting value is considered to correspond to the distance of discontinuous crack advance under normal constant-load conditions. Note that if propagation were continuous, Δx would decrease continuously to zero. Studies of the dependence of Δx on Δt have now been extended to alpha-brasses and to the Al-Zn-Mg alloy to determine the generality of the effect. Another key mechanistic issue concerns the role of hydrogen in the stress-corrosion process, and work was started to study both alpha-brasses and the Al alloy. In the latter case, the occurrence of internal hydrogen embrittlement is well established, and work was initiated to compare the characteristics of this phenomenon with those of conventional stress-corrosion cracking. In the case of the brasses, work has been started to establish whether hydrogen embrittlement can in fact occur in copper alloys.

(4) Two new joint research efforts were initiated in FY80 with other Divisions in the Center for Materials Science. Both of these projects have as their aim the development of a better understanding of how alloy composition and structure affect the passive layers that control corrosion processes. The first is in collaboration with Dr. D. M. Sanders of the Ceramics, Glass, and Solid State Science Division. It is concerned with determining the role played by alloying elements in influencing the properties, especially structure, of passive films. The work uses the new apparatus built by Dr. Sanders and his colleagues that is capable of producing synthetic oxide films of different compositions and being capable of in situ analysis of such films using four different surface analytical tools. An electrochemical method for evaluating the ability of passive films to resist breakdown has been set up. The second research program initiated is in collaboration with Drs. M. Kuriyama and G. G. Cohen of the Metallurgy Division. This work is aimed at using synchrotron radiation to study passive films on metal surfaces. Work has been started to study the passive film on copper, iron, and chromium using EXAFS.

(5) Efforts to control the corrosion of steel in chloride contaminated concrete using new protection techniques being developed by Government and industry have been hampered by the lack of a nondestructive method for measuring the corrosion rate of steel in concrete. This measurement of corrosion would allow an evaluation of the effectiveness of the various protection systems. During the past year considerable progress was made on a project for the Federal Highway Administration that seeks to develop a technique for measuring the corrosion of steel in concrete. During the first year of this work, four polarization techniques were used to measure the corrosion of steel in concrete. These four polarization techniques were chosen as a result of a critical review of the literature (NBS Special Publication 550). These techniques, (Stern and Geary's linear polarization, Mansfeld's polarization resistance, Barnartt's three point method, Schwerdtfeger's break in the curve), were applied to several concrete slabs (60 x 30 x 5 cm) each containing three steel bars. Because of the high resistivity environment of the concrete, it was necessary to compensate for the IR error generated during polarization. The weight loss calculated from these electrochemical measurements was compared to gravimetric weight loss measurements of the bars. It was found that the Stern-Geary method gave the best agreement with actual weight loss. Progress has been made toward developing a microprocessor controlled instrument to make the polarization measurements in a simple automatic fashion in the field. A parallel study on the effect of Cl concentration, oxygen concentration, pH, and moisture content on the corrosion of steel in concrete revealed that it is necessary that the chloride contaminated concrete go through a drying cycle to initiate the

corrosion of steel. This concentrated the chloride and oxygen sufficiently so that film breakdown occurs. Once this takes place, the corrosion process lowers the pH locally allowing corrosion to continue.

(6) A new project under the sponsorship of the Electric Power Research Institute (EPRI) was started in October 1979. This project continues work originally supported by Department of Energy (DOE) that seeks to develop test methods for the detection of dangerous corrosion conditions that can exist when cables for the transmission of electric power are installed underground. Since such underground cables have been in use, their copper concentric neutral wires have been found to undergo corrosion in a number of installations. This new project seeks to evaluate the applicability of polarization and electrochemical noise measurements as *in situ* methods to detect concentric neutral wire corrosion.

The new EPRI project's work on the evaluation of the polarization method has involved the installation during the past year of two sets of 50 m cables at a test site on the NBS grounds. Each set is made up of two parallel 50 m cables. Imposed on the concentric neutral wires of one set is an ac signal sufficient to develop a current density of $1 \mu A/cm^2$ to ground simulating an operating cable. The second set is ac free. The corrosion of both sets was measured by polarization techniques, and indications are that the cables with ac are deteriorating at a greater rate than those without imposed ac. The distribution of current over the cable during polarization has also been investigated. The current distribution is important since it is necessary for the calculation of corrosion current density.

Automation of the measurements at the field site by personnel in the Electrical Measurements and Standards Division has progressed to the point that an automatic IR compensating circuit has been developed and made. It incorporates a modification of the Wheatstone bridge in a Holler circuit using a variable voltage source to produce a bias voltage in one of the legs of the bridge for balance. Results using a dummy circuit to simulate a corroding cell indicate that IR balance is achieved with 0.1 to 0.5 mv error. A mobile field laboratory is in the process of being placed at the test site to house the automated equipment.

The stability of three types of permanent solid reference electrodes has been measured. Of the three ($Zn/ZnCl_2$, $Cu/CuSO_4$, Zn), the $Zn/ZnCl_2$ has maintained a stability of ± 0.0004 V over a 60 day period. The bare zinc electrode has shown the least stability at ± 0.060 V over the same period. New electrodes have been made containing a small (0.1 to 1.0 percent) concentration of $HgCl_2$ which may improve long-term stability.

Polarization and current distribution measurements have been made on operating cables owned by Prince William Electric Cooperative, Manassas, Virginia. The ac interference on our instrumentation has practically been nonexistent with a maximum level of 1.5 mV peak to peak. The measurements have been made without any serious technical problem.

The work in electrochemical noise measurements has developed an approach that enables the identification of which part of the corrosion current is the response to input voltage signals and which part is caused by random fluctuations characterizing the corrosion of the copper concentric wires. Laboratory measurements on copper concentric wires embedded in agar to simulate conditions in the soil have been started.

(7) Work has been completed on a Department of Transportation (DOT) project that has used the slow strain rate test to determine the susceptibility of pipeline steel to stress corrosion in carbonate/bicarbonate solutions. Smooth and notched round specimens were tested at room temperature in a 1 N carbonate/bicarbonate solution at strain rates of 10^{-4} to 10^{-7}/s. The slow strain rate test was also modified to provide cyclic loading around a set load. None of the specimens tested indicated susceptibility to stress corrosion cracking. For comparison purposes, several fracture mechanics compact tension specimens were tested in the laboratory as well as being field tested in two underground burial sites where the two soils have different corrosive properties. A final report of this project has been completed.

Evaluation of Corrosion Resistance of Materials: This area has as its objective the production of new corrosion resistance data of materials (primarily metals) in environments of practical importance. As a consequence of pursuing this objective, test methods are sometimes developed or those developed in the previously described area are adapted.

Significant technical activities during FY80 in the evaluation of the corrosion resistance of materials have been the following:

(1) Progress continued on a project supported by DOE to assess the corrosion resistance of candidate alloys for downstream components of MHD systems. Using a simple burner rig, tubular specimens of Type 304 and Type 316 stainless steel were exposed to a seeded oxygen-propane fueled hot gas stream under varied conditions of temperature, seed composition, and propane-oxygen ratios. The specimens were subsequently analyzed by optical, SEM and EDX techniques for signs of incipient or gross corrosion. In addition, some aspects of the geometry of the seeded deposit on the specimen surface were determined.

Specifically, the specimens were stream seeded with K_2SO_4 or with K_2CO_3. Internal cooling maintained the specimen at either 400 °C, 500 °C or 590 °C in a fuel-rich or oxygen-rich hot gas stream; local temperature at the specimen was approximately 1300 °C.

In every instance some degree of non-uniform attack was observed. Generally the attack was most severe on the surface of the specimen facing the hot gas stream. This area was also coated with a compact deposit, the thickness and character being dependent on the exposure variables. The remaining surface, the downstream side, was coated with a thinner, powdery type deposit, also dependent on exposure variables.

SEM and EDX analysis of the interface region between the salt deposits, compact or powdery, and the metal revealed reaction zones containing species of the bulk material. In all cases for both Type 304 and Type 316 stainless steel, high concentrations of Ni were detected immediately adjacent to the bulk material. Immediately beyond this is a zone containing a high concentration of Cr followed by a zone containing a high concentration of Fe with some cases of no evidence of Ni.

In the coming year the evaluation of materials as described will continue.

(2) Since 1967, the National Bureau of Standards under the sponsorship of the American Iron and Steel Institute has been involved in a study of the effectiveness of corrosion protection of steel in sea water by a variety of systems. These systems consist of metallic and nonmetallic coatings, single system and two system coatings, and cathodic protection of bare and coated steel. The degree of protection afforded by these systems is measured annually using electrochemical techniques in conjunction with visual and photographic records.

The annual on site evaluation develops data that lead to a better understanding of the deterioration rate of these protection systems. These data are then compared to the physical measurements made on piles that have been extracted from the site for study.

These data show, for example, that coal tar epoxy alone is undercut and damaged relatively fast, but when the same epoxy is used as an overcoat on a zinc-rich inorganic silicate coating, both benefit, and the combination is very resistant to attack.

(3) Historically, 5-mil copper has been used as a shield material in non-gopher infested areas with 10-mil copper being used in areas requiring gopher protection for telephone cables. Bi-metallic shields using copper and stainless steel have also been used in lieu of 10-mil copper. Due to an increase in underground telephone cable installation coupled with increasing cost and fluctuating availability of copper, a program was initiated by NBS and the Rural Electrification Administration (REA) to develop and investigate metals or combinations of metals and other materials for use as a substitute for copper in buried telephone cables. REA estimates that the NBS work has an impact on 90 percent of the $600 million industry producing and using the telephone cables, whose design is based on the NBS program.

The corrosion behavior of many different shield systems utilizing other metals or alloys and composite metals and plastics has been investigated over a six-year period at six NBS soil corrosion test sites. Since initiation of the program, it has been expanded to include additional systems. These systems are representative of advances in technology with respect to manufacturing processes or techniques in addition to the use of new materials.

The results to date show that some of the cable systems utilizing aluminum alloy shields with ethylene/acrylic acid copolymer film coatings provided good protection to the cable core in some of the less aggressive soils. However, when coupled to copper, their performance was poor in one more of these soils. Good protection was afforded in all of the soils by systems incorporating a Type 304 or Type 430 stainless steel outer shield with an aluminum alloy inner shield separated by a polyethylene jacket.

Systems buried up to six years have been evaluated and a report containing the results obtained from these tests should be completed in the fall of 1980.

In 1977, this program was further expanded to include "buried plant housings" which are used in the construction of telephone systems. Representative samples, to be investigated over a six-year period, were exposed at four of the NBS soil corrosion test sites and at two additional sites (one, in northern Pennsylvania and the other along the seacoast in South Carolina). Removal of the second set of "plant housings" exposed for two years has been completed at five of the six soil sites. Exposure of additional samples, representative of advanced technology in materials fabrication has been initiated.

(4) Stainless steels have been proposed for use in underground applications such as gas, water, telephone and electrical distribution systems, ground rods, culverts, transformer cases, residential sewage disposal, etc. In 1970, an investigation was initiated with partial support from the American Iron and Steel Institute at six NBS soil test sites to evaluate the corrosion behavior of stainless steels in underground service. This was expanded in 1972 and 1973 to include materials representative of newer alloys. Aspects being studied include general corrosion behavior, pitting and crevice corrosion, stress-corrosion cracking, and hydrogen embrittlement. To date 1054 specimens have been buried at each site for a total of 6324 at the six test sites. The exposure periods chosen were one, two, four, eight, and X years. A report containing the results obtained from specimens buried up to eight years has been completed and the project has been terminated.

(5) With the support of DOE and the NBS Office of Recycled Materials, a study has been initiated on the corrosion of metals and alloys used or under consideration for use in waste-to-energy systems. This study is directed toward corrosion problems that may exist in incinerator systems where refuse-derived fuels are manufactured. To date, NBS personnel have made on site visits to several incinerators in order to determine existing problem areas and to obtain samples (if available) for analysis. Future plans include the placement of candidate materials in the form of metal coupons in incinerator systems which can be monitored on a regular basis in order to determine their corrosion behavior.

Electrodeposition: This area seeks to develop new understanding of the structure of electrodeposits and electrodeposition processes, to improve current electrodeposition technology, to produce and develop new SRM's that are necessary for the measurement technology used by the plating industry and to devise new SRM's, requiring electrodeposition for their fabrication, for use in nondestructive evaluation techniques.

Significant technical activities during FY80 in this area have been the following:

(1) The three-year project for the Aluminum Association directed at obtaining a better understanding of the factors that affect adhesion and corrosion of electrodeposits on aluminum was completed during the past year. Among a number of accomplishments achieved during the past year the following two were most noteworthy:

(a) In work directed at obtaining a better understanding of the effect of anodizing parameters on the adhesion of electrodeposits on Al, it was shown that adhesion is an approximately linear function of the applied voltage. Since the pore diameter (and the cell diameter) also increases in a linear manner with the applied voltage, a relationship was thought to exist between adhesion and pore diameter. Moreover, the greater the pore diameter, the less oxide there is per unit area of the coating. This implies that the strength of the oxide itself is the determining factor (or weak link) in adhesion of subsequent coatings to the anodic film. It should be noted that the pore structure, especially at higher voltages, does not vary much as one changes from one of the three major electrolytes used for this process (sulfuric acid, oxalic acid, and phosphoric acid) to another. Therefore, the adhesion does not appear to be dependent upon the pore structure, but, rather, upon the strength of the oxide itself and upon the percentage of oxide coverage of the surface. The composition of the anodic film varies considerably with the alloy and with the electrolyte. Therefore, the microstructure of the oxide itself (not the pore structure) and its composition are the determining factors.

(b) A theory which predicts the adhesive energy for metallic coatings on metallic substrates was developed. The theory takes into account the effect of structure through a parameter "a" which represents the lattice parameter <u>in</u> the interface. This parameter is determined by the orientation of both the substrate crystal and the coating crystal. The adhesive energy as a function only of the structure is

$$E_{ad} = \frac{K\,G_o\,a^2}{(2\pi)^2 d} \quad . \qquad [1]$$

For f.c.c. materials, K = 3. G_o is the shear modulus in the interface which can be determined from the binding energy between the two metals and d is the distance of closest approach. The lattice parameter in the interface is given by

$$a = \frac{2a_c\,a_s}{a_c + a_s} \quad . \qquad [2]$$

where a_c and a_s are the (orientation dependent) nearest neighbor distances in the coating and substrate respectively. In many cases perfect epitaxy is not possible; therefore, the misfit between the coating and the substrate has to be taken into account. It was shown that the adhesive energy in the case of significant misfit is given by

$$E_{ad} = \frac{K\ G_o\ a^2}{(2\pi)^2 d} - Ed \qquad [3]$$

where E_d is the dislocation energy per unit area. As a result of misfit between the substrate and the coating, strains will be produced so that the equations for adhesion must be further modified. In the case of significant stored energy, the adhesive energy is given as

$$E_{ad} = \frac{K\ G_o\ a^2}{(2\pi)^2 d} - E_d - E_s \qquad [4]$$

where E_s is the strain energy. A special case was calculated for zinc coatings on aluminum whose epitaxial relationahips were characterized during this program.

(2) Each year some investigations and development are conducted as a back up to the Standard Reference Materials (SRM) program. This year a new x-ray spectrometer was evaluated for the measurement of coating thickness. This involved designing and testing specimen holders, and determination of the measurement precision for various coatings. Computing equipment used for the coating thickness measurements has been upgraded. Also the density of some autocatalytic Ni-P alloy deposits was determined with a new piece of equipment owned by the Density Measurement group at NBS.

(3) Work has continued under the sponsorship of the NBS Office of Nondestructive Evaluation on the development of dye penetrant sensitivity crack panels by electrodeposition. Alternate layers of nickel and copper are electrodeposited on a nickel sheet so that a cross section of the laminate electrodeposit shows thin copper lines between bands of nickel. The copper is then partially dissolved leaving deep cracks. Crack panels made this way can be used to evaluate an important NDE crack detection method. A number of crack panels have been produced and given to other laboratories for evaluation. Each panel is about 1/2 x 2-1/2 cm with four parallel cracks running the length of the panel. The four cracks are nominally 0.2, 0.6, 1.0, and 2 µm in width and several times deeper than wide. Similar crack panels will become SRM's when the evaluation reports come in with recommendations relative to crack widths, panel size, panel mounting, etc.

(4) A simple chemical immersion technique has been developed which produces ultra-black surfaces on electroless nickel-phosphorus coatings. A patent on this development was granted this year. The blackness is associated with a unique surface morphology consisting of a dense array of microscopic conical pores (2-9 µm average diameters) perpendicular to the surface. This structure is produced by a selective etch with nitric

acid. The unique surface morphology, acting as light traps, is capable of absorbing over 99 percent of the incident light when tested at wavelengths of light from 340 to 2140 nanometers. This extremely high light-absorbing surface can be applied to a variety of substrates, such as metals, ceramics, glass, and plastics.

Interest in this process over the past year is indicated by over 325 inquiries that have been answered for the application of this coating in space telescopes, laser absorbers, radiometers, black body detectors, solar collectors, low reflectance standards, etc. Four talks were presented and four papers were published, as well as news briefs appearing in trade journals, newspapers, and scientific magazines covering a broad scope of interests from optics, solar energy, astronomy, and space physics to materials and coatings research.

(5) Work continued in the production of coating thickness SRMs, used to calibrate coating thickness gauges. A single SRM is a metal coupon, 3 x 3 cm or 1.5 x 1.5 cm, one surface of which has an electroplated coating of certified thickness. Most of these are non-magnetic coatings on steel, but also included are nickel, gold, and tin coatings on various metallic substrates. Some 53 different SRMs are made ranging in thickness from 0.7 μm to 2 mm. (Gold coatings are actually certified in units of mass/area, not length.) They are designed for use with either magnetic type or beta backscatter type thickness gauges.

These SRMs are packaged in sets and the SRM catalog lists some 31 different sets. About 3000 individual coating thickness standards were produced during FY79, and about 5000 were produced during FY80.

Chemical and Biodegradation Processes
Subtask 2 of Task 12111

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The technical activity of this subtask is focused on measurement and mechanistic characterization of chemical and biological processes involved in the transformation and degradation of materials. Underlying the multidisciplinary approach taken by the Group is the recognition that both chemically and biologically mediated processes are significant factors in corrosion and degradation of materials in natural service environments. The current work in the task seeks to concentrate on a few topical problems of major importance involving metal-containing materials. Emphasis is on assessing roles of organometallic substances in materials transformations and degradation because of the widespread use of organometallics in world technology and the significance of organic derivatives in the degradation, mobilization, and transport of metallic elements through the environment. The work in this subtask falls into several areas with two primary foci: the development of compound-specific methods for detecting, identifying, and quantitating organometal species at environmental concentrations (μgL^{-1} to ngL^{-1}); and the application of this methodology for characterization of the degradation of materials in service environments.

Speciation of Organotin Monomers: The durability and environmental impact of organotin materials are of current interest because of the widespread use of these substances as antifoulants, biocides, and polymer stabilizers and recent demonstrations of their widespread occurrence in the environment.

The speciation of R_3Sn^+ ions by high performance liquid chromatographic separation techniques using strong cation exchange (SCX) columns coupled to tin-specific graphite furnace atomic absorption (GFAA) techniques, reported in FY78-79, has been expanded to include the tricyclohexyltin ion and separations have been improved to provide increased column efficiencies and reduced elution times. An extension of this work to include speciation of more highly retained R_2Sn^{2+} species (R = butyl, phenyl, ethyl) has been developed. Moreover, the selectivity of the SCX column is such that facile resolution of isomeric organotin species was accomplished.

A major accomplishment in FY80 was the development of a quantitative relationship between the chromatographic behavior and molecular substituent properties, derived from measurements physically independent of chromatography, for several classes of organotin compounds. This relationship permits: (1) accurate prediction of optimal chromatographic conditions for known organotin ions, or (2) identification of unknown R groups on organotin compounds. After conducting analysis with various molecular substituent constants in the literature, the constant selected for this study was σ^{Φ}, which represents combinations of both inductive (σ_I) and $p\pi$ or $d\pi$ resonance (σ_R) effects that may occur with energetically available p or d orbitals in R-Sn bonding. The relationships of the natural logarithm of the chromatographic capacity factor, k', versus independent literature values of σ^{Φ} for the various classes of organotins is indicated in figure 1. Detection limits of 16 ng, 5 ng, and 26 ng, respectively, for Bu_3Sn^+ ($r = 0.993$), ϕ_3Sn^+ ($r = 0.997$) and $(Cyhx)_3Sn^+$ ($r = 0.979$), were determined experimentally from calibration curves. Differences in detection limits for the various species were probably due to the relative atomization efficiencies of each species in the graphite furnace.

Application of this technique to a problem of environmental concern provided significant information. At various naval dockyards, the "spent" organotin (tributyltin) antifouling coating on ships is removed by grit blasting. This material (grits plus coating particles) which still contains large amounts of organotin (R_3Sn^+) biocide presents a disposal problem. Direct examination of the water leachate of this material by the HPLC-GFAA system indicated the presence of both Bu_3Sn^+ and the less toxic Bu_2Sn^{2+} (about twice as much), the latter being a decomposition product of Bu_3Sn^+. These results are the first specific demonstration of a decomposition pathway for tributyltin and clearly suggest a valuable monitoring tool.

Speciation of Organotin Volatiles from the Chesapeake Bay: Several organotin species, especially the methylated species, reported to be present in natural waters and urine are believed to be biologically produced from inorganic tin. The volatility of these materials permits the use of gas chromatographic techniques. Last year, modifications were made to a commercial flame photometric detector (FPD), which allowed volatile tin species to be detected at pg levels. Samples of headspace gas above bacterial cultures were analyzed and volatile tin metabolites were detected. It was also desirable to analyze the presence of aqueous samples to determine the presence of dissolved volatile tin species. For this purpose, a purge and trap sampler was retro-fitted to the GC system for use with the FPD. Developed for the Navy (ONR), this system can be used aboard ships for on-site monitoring.

In the purge and trap sampler, an inert gas, He or N_2, is purged through the liquid sample to drive any dissolved volatile compounds from the liquid into the headspace. The volatiles driven into the headspace are collected at ambient temperature on a trap filled with Tenax GC, a polymer which retains the volatile species. The Tenax trap is quickly heated to a high temperature to introduce the collected volatiles into the gas chromatograph where they are separated on the column and detected by the FPD. Methylated sulfur compounds (i.e., dimethyldisulfide and methylsulfide) are naturally occurring microbial metabolites found in sea water and could therefore interfere with the tin response since sulfur can also be detected with the present FPD system. Tin calibration curves for several interference filters were therefore made using standard solutions of Me_4Sn/Me_2S and Me_4Sn/Me_2S_2 in deionized water and sea water. Detection limits ranged from 30 to 50 ng/L. but will be improved ten-fold with new photomultiplier and improved calibration techniques.

Field water samples collected from the Chesapeake Bay (Baltimore Harbor) were analyzed for volatile organotin species using the Purge and Trap/GC-FPD technique. Results of these analyses indicated the presence of tetramethyltin in the Bay water. By using the method of additions, as much as 900 ng/L of Me_4Sn may be detected in Colgate Creek in Baltimore Harbor. Partition coefficient measurements of Me_4Sn will be necessary, however, to determine the concentrations of Me_4Sn more accurately in aqueous media.

Speciation of Arsenic Compounds in Oil Shale Process Waters: The extraction of shale oil from substantial deposits of oil shale has emerged as a viable fossil fuel alternative. Current recovery procedures produce, along with shale oil, considerable amounts of process waters which contain many organic compounds as well as trace metals and metalloids in forms that are potentially toxic to aquatic biota and man.

As part of a joint effort between Chemical and Biodegradation Processes Group personnel and members at Lawrence Berkeley Laboratory's Oil Shale Program, a research program which seeks to characterize metal toxicants present in various process waters of representative recovery procedures was initiated. Compounds of arsenic were selected for study because substantial concentrations of total arsenic (0.3 - 15.5 ppm) had been measured in process waters, and some inorganic arsenic compounds are suspected of being carcinogenic.

In the course of exchange visits between LBL and NBS, seven oil shale process waters, including samples from simulated, true or modified in situ processes, were speciated for inorganic and organoarsenic compounds. High performance liquid chromatographs automatically coupled to graphite furnace atomic absorption spectrometers were employed in both laboratories. The molecular forms of arsenic contained at ppm levels in these waters were identified for the first time and shown to contain arsenate, methylarsonic acid, and phenylarsonic acid, figure 2. The chromatograms for each process water studied have significant implications regarding those arsenic species found and those not and/or marginally detected (such as the possible carcinogen, arsenite), as well as quantifying future environmental impacts for such bioactive species involved in oil shale retorting technology.

Size-Exclusion Characterization of Biocidal Organotin Polymers: Organometallic polymers (OMP's) incorporating triorganotin varieties, chemically bonded to carboxyl groups pendant along polymer chains are undergoing intensive development as long-term controlled release, marine antifouling coatings. In use, organotin moieties are slowly leached out of the coating to provide the fouling inhibition effect. To devise a useful and predictable slow release OMP, it is desirable to incorporate most of the organotin within a high polymer matrix.

Size exclusion chromatography coupled with tin specific graphite furnace atomic absorption spectroscopy (SEC-GFAA) has been developed to the point of characterizing high and low polymer fractions of OMP's. Significant characteristics obtained include molecular weight average, number average, molecular weights, molecular weight distribution, and the percent of tin found in each of the major fractions. It has been demonstrated that a large number of OMP's include 10 to 20 percent of the total Sn in a low Mw fraction. The presence of the low Mw tin-containing species in these high concentrations is undesirable from the point of view of controlling the rate of release of toxic moieties in service environments. However, the nature of the material and its source are uncertain. These materials could be unreacted tributyltin methacrylate (TBTN), unconverted tributyltin oxide (TBTO), or decomposition fragments.

In addition to these studies on the developed OMP's an investigation of the kinetics occurring during the copolymerization (methyl methacrylates and organotin-substituted methracylates) of these materials by both SEC-GFAA and FT-NMR of the Sn nucleus has been initiated (figure 3, 4). This is the first metal-specific use of the NBS Hi-Field FT-NMR facility.

Evidence indicates that the signals from the monomer and polymer are well separated so that kinetic information, not previously obtainable with studies of the H nucleus, can now be obtained.

Microbial Volatilization of Mercury by Thiobacillus Ferrooxidans: In the mercury geochemical cycle, mercury is found principally as the sulfide ore, cinnabar(HgS) and is believed to be trapped in polluted bodies of water as the sulfide. Although it has been suggested that mercury can be released from sulfide by biological action, there is no reported evidence of this process. Since a bacterium, *Thiobacillus ferrooxidans* has been repeatedly demonstrated to solubilize metals from their sulfide ores, this organism would also appear as the logical choice for its capacity to solubilize mercury from such ores.

T. ferrooxidans is an economically important iron and sulfur-oxidizing, acidophilic bacterium which contributes to the production of acid coal mine wastes by the production of sulfuric acid through the oxidation of iron pyrite (FeS_2) and other metal sulfides. Conversely, its highly beneficial activities involve the leaching of many metals from their sulfide ores. Little is known of the action of *T. ferrooxidans* on mercury, however, despite the fact that mercury often occurs associated with coal and metal ore deposits containing mercury.

In investigating the effect of mercury on *T. ferrooxidans*, it was found that populations of this organism, normally quite mercury sensitive, readily develop tolerance to Hg^{2+} ions, and, furthermore, have associated with this tolerance the capacity to volatilize the Hg^{2+} ions by reduction to elemental mercury (figure 5). This is the first demonstration that autotrophic bacteria can bring about this reaction, although it is quite common in heterotrophic bacteria. Mercury volatilized in the latter group of bacteria is usually plasmid (extrachromosomal DNA) mediated. Preliminary evidence has, however, failed to indicate any plasmid DNA in this organism.

Microbial Tolerance and Uptake of Organotin Biocides: The use of organotin compounds as antifouling agents in coatings for marine use is expected to increase. Since it has been demonstrated (above sections on speciation) that the highly toxic tributyltin moiety is leached from an organotin polymeric coating, it is of concern from an environmental standpoint to determine the fate of such a compound in biological systems (i.e., conversion to a more or less toxic moiety or sorption which may be physically, chemically or biologically mediated).

Six naturally organotin (tributyltin) resistant bacterial strains obtained from Dr. R. Colwell (University of Maryland), (isolated from the Chesapeake Bay and Newport Bay, California sediments) were grown in the presence of 10 ppm of tributyltin chloride in a low sulfur medium. Analysis of the cell-free medium by the HPLC-GFAA tin specific system after various periods of time showed no evidence of tributyltin degradation (i.e., no other tin moieties could be detected). Analysis of the cell-free medium by the Purge and trap/GC-FPD has, however, indicated the presence of a volatile tin species.

In studies with the six organisms, it was found that the cells accumulated significant amounts of tributyltin (c., 0.6 to 2.2 percent of the total organotin present in the medium). Studies are in progress to determine whether the tin uptake is simple sorption or whether it is biologically mediated.

Stability Testing of NBS SRM's: A project concerned with the establishment, of a measurement protocol which permits quantitative assessment of the nature and extent of their biodeterioration potential under present NBS certification procedures, was initiated. This project will be sponsored by the current and future NBS programs. With respect to potential biodegradation, results have indicated that the SMR's may be divided into three categories:

(1) sterile as received [viz., oyster tissue (SRM 1566), river sediment (SRM 1645), orchard leaves (SRM 1571), and brewers yeast (SRM 1569)];

(2) sterile as received but contaminated by recommended handling procedures [viz., freeze-dried urine (SRM 2672)];

(3) not sterile [i.e., urban particulate (SRM 1648)].

Brewers yeast, oyster tissue, and orchard leaves exposed for a total of three and one-half hours at one-half hour intervals to the outside air and maintained at 25 °C, 90 percent relative humidity, became badly deteriorated, largely as a result of fungal attack.

Biomethylation of Inorganic Tin: It has been previously reported by NBS (C. Huey, F. E. Brinckman, S. Grim, and W. P. Iverson; Proc. Inter. Conf. on Transport of Persistant Chemicals in Aquatic Systems 1974) that a volatile methylated tin species was produced by a *Pseudomonas* strain (#244) from the Chesapeake Bay. Re-examination of the headspace from this culture growing in the presence of Sn^{4+}, using a GC-MS system, revealed the presence of two methylated tin species, one presumably tetramethyltin and the other possibly trimethylstannane, Me_3SnH.

Anaerobic Corrosion of Iron: Anaerobic corrosion of iron occurs throughout the world and from an economic standpoint, is quite costly. Sulfate reducing bacteria, primarily of the genus *Desulfovibrio*, are responsible for this type of corrosion. It has been postulated that corrosion by these bacteria is caused by their removal of hydrogen from the surface of iron, causing the iron to go into solution.

Evidence was obtained which indicated that this mechanism may not be responsible for the main corrosive effect of these organisms. Corrosion by these bacteria has been demonstrated to be caused by a volatile sulfur containing metabolic product which is not H_2S. Evidence for at least four sulfur containing metabolites from this organism has also been demonstrated.

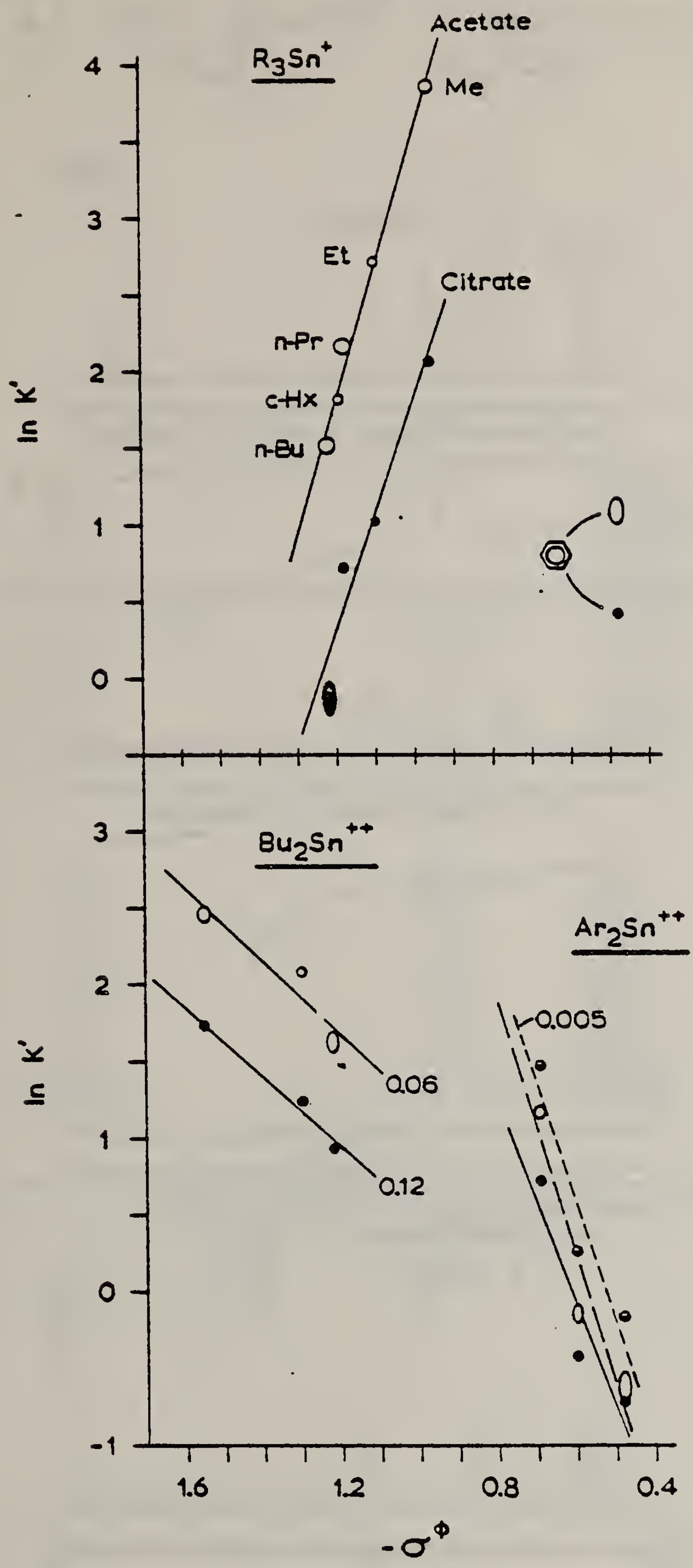

Figure 1. Linear relationship between the substituent constant σ for R groups on various organotin in two buffered solutions (citrate and acetate) and the logarithm of the observed capacity factor k'. Anomalous behavior for triphenyltin is apparent in both buffers. Indicated in the lower plots are, t-βu, i-βu, and n-βu (descending order) in two citrate buffer concentrations, and Ar = tolyl; para-tolyl; and benzyl (descending order) in three citrate buffer concentrations. (0.005 M, 0.0075 M, and 0.01 M, right to left).

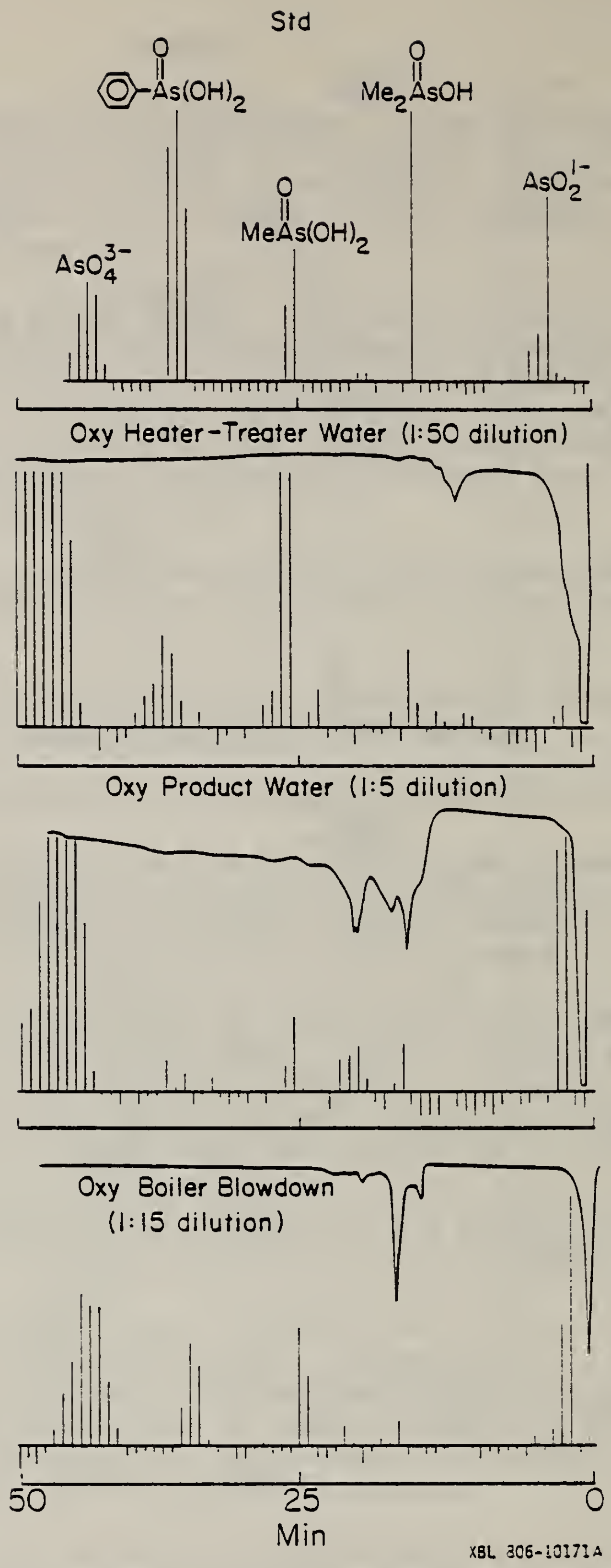

Figure 2. Element-specific chromatograms or arsenic species fingerprints obtained by HPLC-GFAA (bottom of each sample set) and associated UV detector chromatogram (continuous trace shown at top, inverted) are compared against standards for three water samples taken at different stages of the Occidental Modified <u>In Situ</u> Process, Retort 6, Logan Wash, Colorado.

SEC-UV-GFAA CHROMATOGRAMS OF AN OMP AT TWO STAGES OF REACTION

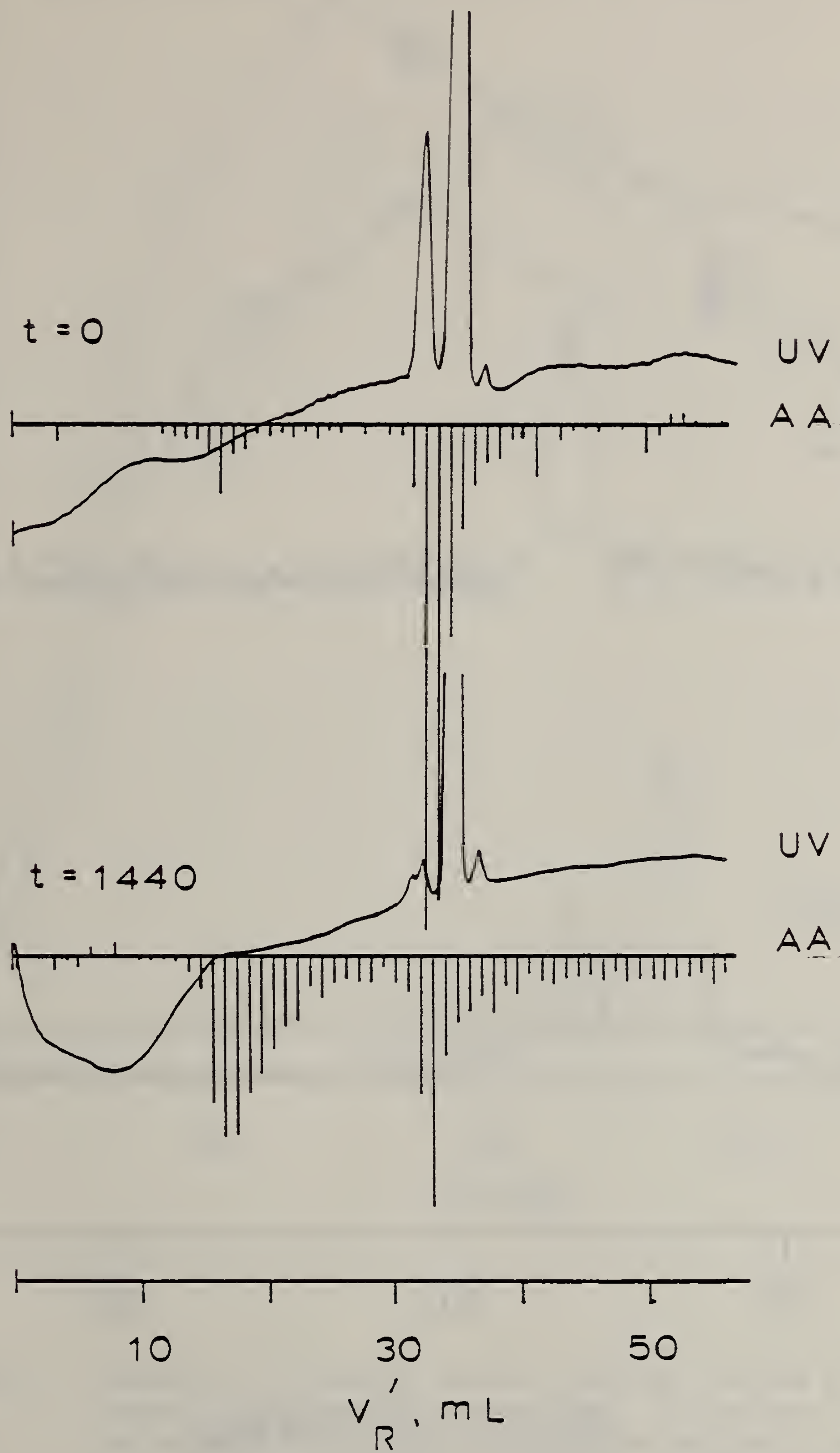

Figure 3. The changes in UV and Sn spectra are followed initially and after 24 hours; during the conversion of tributyltin methacrylate in the presence of methlmethacrylate and a free radical initiator. The ratio of high (low retention volume $[V'_R]$) to low (high $[V'_R]$) molecular weight species increases with respect to time.

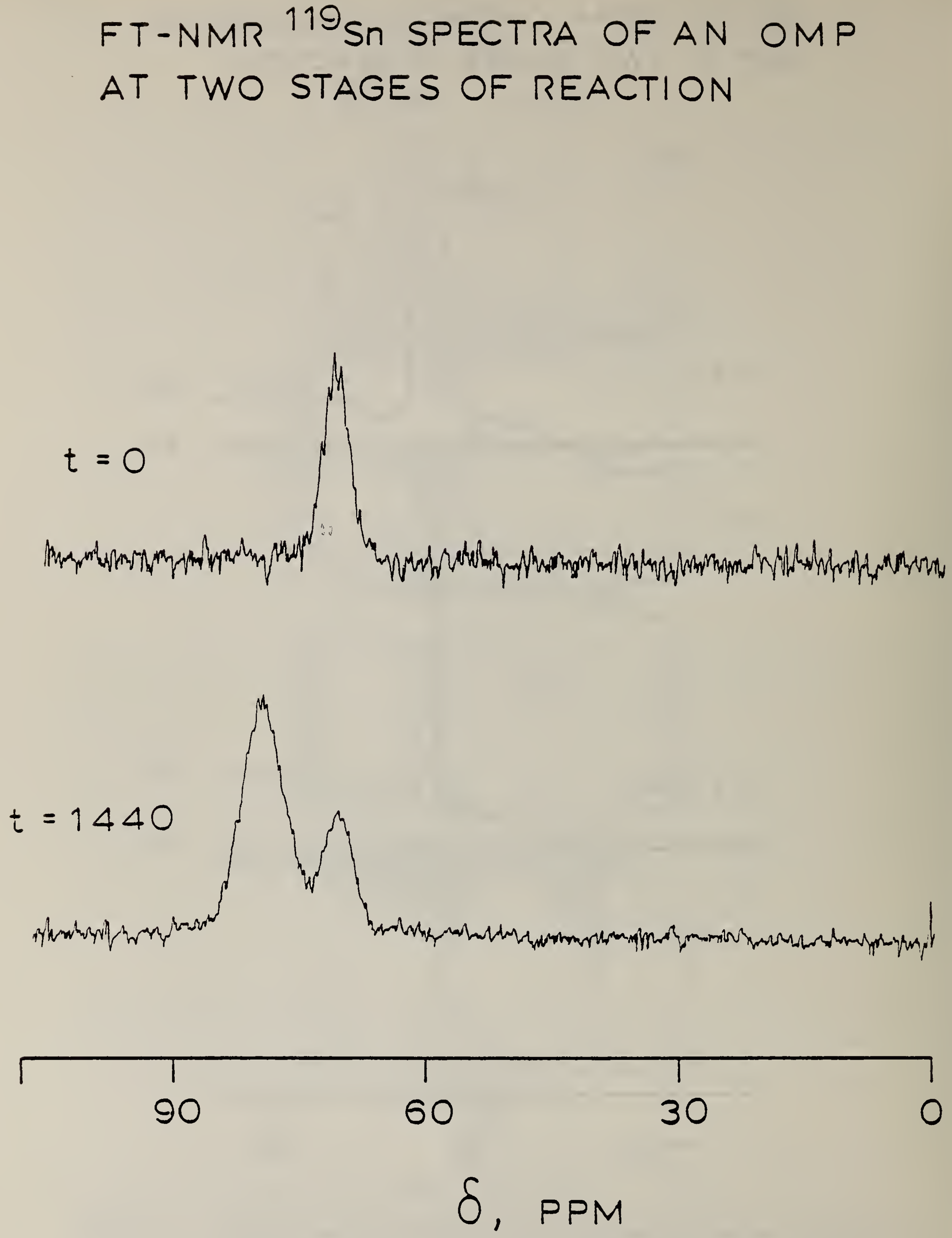

Figure 4. Changes in FT-NMR ^{119}Sn spectra during the same reaction as shown in figure 3.

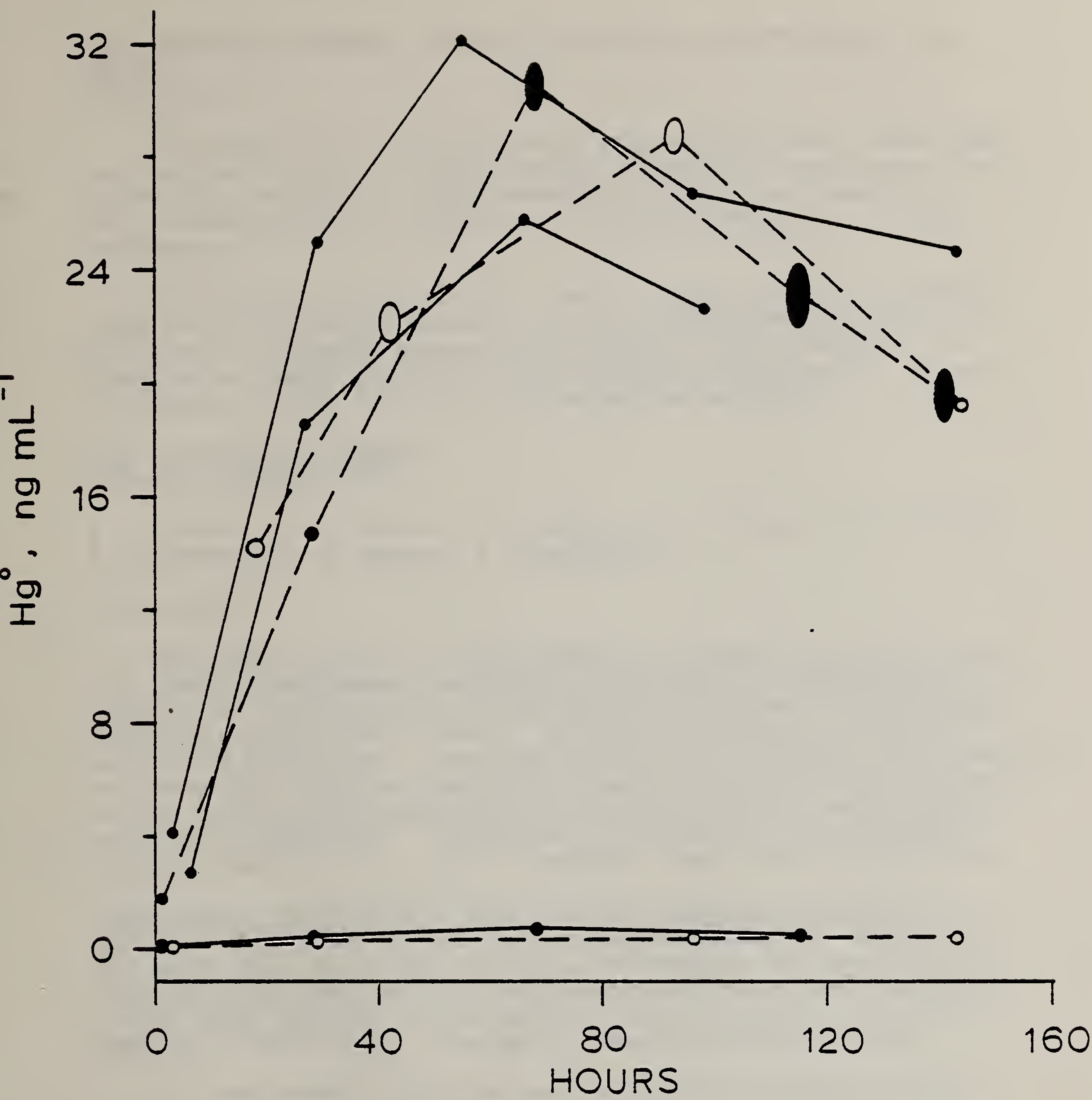

Figure 5. Formation of elemental mercury from Hg^{2+} by the autotrophic Bacterium Thiobacillus Ferooxidans. The bottom curves indicate the response of the mercury unadapted sultures (--●--) and the organism free control (--O--). The top curves show the responses of the mercury adapted culture (0.6 ppm Hg^{2+}); four separate experiments.

HIGH TEMPERATURE CHEMICAL STABILITY OF MATERIALS FOR PROCESSING AND SERVICE
Task 12112

The objectives of this task are to provide measurement methodology, test methods, and data related to chemical durability, performance, and processing of materials in high temperature service environments, as well as methodology for prediction of long-term performance in those environments.

The technical activities fall into two subtask areas. One subtask emphasizes heterogeneous processes involving interactions of materials with agressive (usually gaseous) high temperature environments. The other subtask emphasizes solid-state structural considerations and mass and charge-transport processes in high-temperature solids.

<u>High Temperature Processes</u>
<u>Subtask 1 of Task 12112</u>

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Technical activities in this subtask are aimed at developing molecular specific experimental methodology and theoretical modeling tools to characterize the interactions of materials with aggressive gaseous high temperature service environments. Such characterization is critical for performance predictions in new high technology applications (coal-combustion and conversion, advanced propulsion systems) and for materials processing at high temperatures (chemical vapor deposited coatings, metallurgical, and ceramic processing). Similar activities focus on the chemistry of combustion modification, e.g., by inorganic flame inhibiting additives.

<u>Vaporization, and Chemical Transport in High Temperature Vapors</u>: In this activity, new or improved measurement techniques are developed and applied to the study of the reactions, performance, and durability of slag and ceramic materials in high-temperature process environments, such as those pertinent to the operation of coal gasifier and magnetohydrodynamic (MHD) plants. Problems of immediate concern include:

(1) development of improved methods for identification and quantitative measurement of gas and vapor species in heterogeneous systems at high temperatures and pressures;

(2) defining experimentally and theoretically (through thermodynamic modeling) the degree of alkali seed retention by coal slag under MHD conditions;

(3) determining the durability of candidate ceramic MHD electrode and coal gasifier components with respect to their possible degradation by vaporization and chemical transport in MHD and coal gasifier atmospheres;

(4) obtaining molecular data on the rates and mechanisms of the release of alkali and other inorganic impurities from coal minerals, slags and fly ash, pertinent to gas clean-up technology in advanced multicycle combustion systems; and

(5) defining the mechanistic action of inorganic additives as flame inhibitors and enhancers.

Progress in these problem areas during FY80 is summarized in the following items.

Item (1) The recent development of Transpiration Mass Spectrometry (TMS) has provided a new tool with applications beyond the original application to thermodynamic studies of vapor transport. Supersonic expansion to the low pressure required in the spectrometer results in considerable cooling. The translational temperature in the beam may drop by a factor between 5 and 100. Typically, rotational motions equilibrate rapidly with translation. For diatomic molecules vibrations may relax to within 10 percent of the translational temperature.

One effect of the increased population of low rotational levels of molecules is the marked increase in intensity of the rotational spectra. For diatomic molecules, this enhancement is proportional to T^2. Without a detailed analysis of spectra from high temperature molecules a correct description of their structure and derived thermodynamic functions can be grossly in error. Such errors limit the utility of modeling in combustion, magnetohydrodynamic generation of energy, and other high temperature processes. Consequently, in conjunction with the Center for Thermodynamics and Molecular Science, a Stark-modulated microwave absorption cell has been coupled to the Transpiration Mass Spectrometer to obtain structures for high temperature species. The near room-temperature gas molecules, CH_3CN and CH_3F, of known structure were used to investigate beam formation and system behavior. Experiments on the high temperature test molecule, NaCl, were initiated but cooled detectors and signal averaging will be required to produce useful signals.

The "spectroscopically cool" beam source also allows investigation of the recently identified effect of temperature dependent electron impact fragmentation. Fragmentation, which is the splitting of a molecule or ion into smaller units, can lead to misinterpretation of mass spectrometric data if not properly understood. Since the ratio of ion fragments to ion parents is governed by Franck-Condon type transitions between ground state and bound or repulsive ion states, vibrational population shifts can in theory cause significant changes in this ratio. Our earlier work on NaCl beams showed a major temperature dependence in the $Na^+/NaCl^+$ ratio which has been tentatively identified as due to this effect. CsCl is a molecule for which the temperature dependent fragmentation effect has been reported at high temperatures. Under the influence of beam cooling by a factor of five the effect is exaggerated, exhibiting $Cs^+/CsCl^+$ ratios several times larger than the reported high temperature value. Furthermore, the expected strong temperature trend has been found. Further work in this area is being pursued.

Item (2) Current studies in MHD seed-slag vaporization focus on K_2O activity determination in model four-component slags containing K_2O, CaO, Al_2O_3 and SiO_2. Knudsen effusion mass spectrometry is used in this effort. These results are needed to provide a data base for construction of a theoretical/empirical thermodynamically consistent model for prediction of alkali seed retention and/or corrosion properties of real slags produced by combustion of Western sub-bituminous coals. Measurements completed during the current year have demonstrated that SiO_2 and Al_2O_3 have a synergistic effect in reducing K_2O activity while confirming that addition of CaO increases the K_2O activity by orders of magnitude. The NBS-measured activities for K_2O in various slag-like melts are used by many other scientists as reference data.

Vaporization measurements for systems where NaCl was added to K_2O-containing slags showed a rapid exchange between NaCl and K_2O according to the reaction:

$$2\ NaCl + K_2O\ \text{(dissolved in slag)} = 2\ KCl + Na_2O\ \text{(dissolved in slag)}$$

at temperatures as low as 800 K. Sodium and potassium chloride vapor species as well as mixed halide species were observed. These measurements and observations suggest that this process, or one involving other cheap mass produced salts (such as $CaCl_2$), could form the basis of a process for economic recovery or production of the more valuable and costly potassium salts from MHD slags or high potassia (8 wt. %) clay minerals. Chemical thermodynamic data predict large negative free energy changes for these reactions.

Earlier NBS data for potassium vapor pressure over K_2O-SiO_2 melts were fitted to equations which extrapolate properly as required by the Gibbs-Duhem Law. These equations were also constrained to give the NBS-preferred value of the potassium and oxygen vapor pressures over molten pure K_2O. The finally chosen fitted equation reproduces the experimental pressures with a standard error of 13 percent. "Regular" and "non-regular" solution effects were included as well as their temperature coefficients. Beside this empirical fitting, these K_2O-SiO_2 solutions have been modeled by assuming the formation of ideal solutions with compound formation, as has been done by others who claim success. If the presence of only K_2SiO_3 is assumed, there is approximate agreement over a limited temperature and concentration region with the experimental data quoted above. However, if $K_2Si_2O_5$ is also included, the results diverge from experiment by two orders of magnitude. Logically, the model is incomplete without the inclusion of another known compound, $K_2Si_4O_9$. It is evident that the inclusion of this compound would make the comparison even worse, and that this model has severe logical drawbacks and should be discarded.

Item (3) A slightly modified version of the NASA Chemical Equilibrium Calculations computer program has been received and put into operation. Accompanying this was a much larger thermodynamic data bank, which contains 871 species instead of the former number--458. Also 120 species had been updated. SOLGASMIX, our copy of the University of Umeå (Eriksson) computer program for heterogeneous simultaneous equilibria, has been applied to vapor composition predictions in K_2O-SiO_2, slag-hydrogen-water and cement-water systems. A more versatile version of this program has also been obtained and should be operational in the near future.

Item (4) A detailed fundamental examination of coal mineral components in a combustion or coal-gasification environment is being carried out. Vapor transport studies of coal mineral components are in progress. The data will be used in the development of new control and gas clean-up strategies to circumvent problems of corrosion or environmental pollution. The coal-bearing mineral Illite is a clay having major constituents of SiO_2, Al_2O_3, K_2O, and Fe_2O_3 with proportions similar to those in coal ash. Vaporization of Illite samples indicated the release of SO_2, CO_2, Na, and K at relatively low temperatures (< 1200 °C). This behavior is characteristic of the presence of alkali sulfate and carbonate in the Illite samples (at about one percent concentration level). Potassium oxide activities over Illite were observed to agree well with the results expected for a high-silica, high-alumina, low-calcia slag. The activities of SiO_2 and FeO were also determined. The effects of small amounts of H_2O on Illite vapor transport were noted using the Knudsen effusion mass spectrometric (KMS) method. In the presence of H_2 small increases in volatility due to reduction in the O_2 pressure were observed but, in general, the increases in SiO and Fe pressures were much smaller than would be observed if equilibrium were established. Attainment of equilibrium for addition of reactive gases remains a major road- block in the KMS measurements which needs attention. Of special significance is the inability to form KOH(g) from slags when exposed to water vapor because of kinetic effects.

Item (5) In a related study, made in conjunction with Division 565, the effect of H_2O(g) on the vaporization of Na_2SO_4 was monitored using TMS and classical transpiration methods. Our calculated equilibrium thermodynamic predictions favor NaOH(g) as the major gas species. However, the experiments show that this molecule plays no significant part in alkali transport, even when the gas phase contains several percent H_2O by volume. Although a significant loss of alkali might be expected in glass produced with gas-fired furnaces on the basis of the chemical equilibria involved, these results show that equilibrium is not reached. A significant kinetic limitation exists here which is of major importance in glass production and hot corrosion, as well as alkali vaporization from slags.

Item (6) In cooperation with the University of West Virginia, (UWV) and the Morgantown Energy Technical Center the model (coal mineral) compounds sodium and potassium benzoate were investigated with the TMS technique. The decomposition process and the behavior of the decomposition products of these compounds are of interest as models of the ash/alkali organic/inorganic interaction in the production of combustion gases. Material transport in these environments is of critical importance in high technology combustion applications as well as fuel pretreatment processes sucn as coal gasification technology.

Prior to the TMS studies, thermogravimetric analysis (TGA) studies at UWV had identified the presence of two distinct processes in the inert gas decomposition of the alkali benzoates. With ϕCOONa at ~ 450 °C a sharp weight loss occurred and persisted until ~ 550 °C where weight loss ceased. At 775 °C, a new sharp weight loss region was encountered, which terminated at 925 °C. The TMS study led to identification of the species evolved in each of the two regions and the combined vapor pressure versus temperature curves were in good agreement with the TGA data. The first region was assigned as simple decomposition of the benzoate, the major mass spectral ions being $C_6H_6^+$ and CO_2^+. Hence the condensed phase decomposition reaction releases benzene and CO_2 leaving $Na_2CO_3(s)$ and carbon as a char. The second region showed a rapid rise in CO^+ and Na^+ mass spectral signals, indicating the condensed phase reaction:

$$Na_2CO_3(c) + 2C(char) = 2Na(g) + 3CO(g).$$

Item (7) The mechanistic action of phosphorus and halogen-containing additives in flame inhibition and promotion was determined using mass and optical spectrscopic methods. Mass spectrometric measurements of H-atom and other species concentration profiles were made on a near-stoichimetric, premixed, laminar H_2-O_2-N_2 flame containing CF_3Br. The results support

$$H_2 + Br \rightarrow HBr + H$$

as a dominant flame promoting reaction. The effect of HBr on the temperature profile was previously determined using laser Raman spectroscopic methods. Under inhibition conditions, i.e., observed reduction in burning velocity, at a concentration of only 0.005 mole fraction this compound reduced the clean flame reaction zone temperature by as much as 900 K (due to a downstream shift in the reaction zone). On the other hand, a small increase in temperature occurred in the burnt gas region. These effects are consistent with removal of H-atoms in the preflame and reaction zone regions, resulting in a delay of the chain branching process:

$$H + O_2 = OH + O.$$

Virtually nothing is known about the high temperature chemistry of phosphorus in a flame environment. Phosphorus compounds are known flame retardants although the mechanistic evidence is empirical. High pressure sampling mass spectrometry and optical spectroscopic methods have been applied to the molecular characterization of P-containing flames. The species HPO_2 has been identified and found to participate in the key processes controlling flame inhibition and enhancement. The important reactions (forward and reverse) are predicted to be

$$HPO_2 + H \rightleftarrows H_2O + PO.$$

Inhibition occurs for cool flames when the left to right reaction predominates, whereas the reverse reaction, which predominates in hotter flames, causes enhancement. This concept was elucidated from the determined H atom concentrations as a function of temperature and position in the flame. The predicted inhibition enhancement cross-over point of 2350 ± 50 K is in good agreement with the experimental data for a wide variety of flames. It was necessary in the course of this work to estimate the structures and thermodynamic properties of HPO, HPO_2, $NaPO_2$, and $LiPO_2$. The latter two species are significant in the determination of H-atom concentrations using the established Na/Li spectroscopic method. When formation of these species was taken into account good agreement between measured and calculated H-atom concentration data was obtained in the equilibrium (burnt gas) part of the flame.

Characterization Methodology for High Temperature Gaseous Service Environments: Objectives of this activity are to develop and optimize measurement techniques for characterizing high temperature gaseous environments, including flames, and to apply the methodology to assessing and predicting the performance of materials in those environments. During fiscal year 1980 major emphasis has been in development of improved combustion diagnostic techniques and their application to elucidating mechanisms of combustion modification, including flame and smoke retardance.

The role of excited state atoms in both flame ionization and flame chemistry is important, and the use of lasers to alter the excited state population in a flame has become an important combustion probe. In conjunction with the Center for Fire Research, this probe is being used to determine the relative role of neutral atoms versus ions in smoke and particulate formation in an alkali seeded flame. The increased thermal ionization of laser excited atoms (the optogalvanic effect) is used to alter the neutral/ion ratio while a simultaneous scattering experiment measures effects on particulate formation. This uncompleted work is continuing.

In conjunction with the Center for Analytical Chemistry, modeling and additional experiments have been done to study the collection mechanism of ions and electrons from laser enhanced ionization in analytical burners. The results of these experiments have been the determination of effective ionization rates, the mobility of ions in flames, and improvements in probe geometry to assure 100 percent collection of ions formed by laser enhanced ionization. These experiments have shown that even during short laser pulses it is possible to have partial thermalization of the laser excited atoms to even higher energy levels than produced by the laser. The result is a 100- to 200-fold increase in the effective ionization rate for the laser excited level. From an analysis of the response time for the collection of the ions in a flame irradiated by a sharp laser pulse one can determine ion mobilities in the flame environment.

In order to study the efficiency of the collection of the ions/electrons produced by laser enhanced ionization, a new technique for imaging the ionization rates in flames was developed. In this technique the burner is placed between two plates which are held at a high enough voltage difference to collect the ions/electrons on a time scale faster than diffusion, flame drift, or any other factor which would blur the ionization image. A narrow probe, isolated electrically from the plates, is moved along one plate to intercept the flow of electrons/ions locally to the plate. The signal from the probe is then the ionization image as the probe is moved. The probe is about 95 percent efficient in selectively intercepting the current flow from the flame and has about a 1 mm resolution. These experiments are important in designing probes in analytical applications which maximize sensitivity without increasing electrical noise. Since metal atoms, particularly alkalis, are common contaminants in coal slag and increase high temperature corrosion as well as play a role in particulate (pollution) formation, increased sensitivity is important. This increased sensitivity can only be gained with better knowledge of the formation and collection mechanisms pertinent to laser-enhanced ionization.

Recent reports in the literature on laser induced changes in the rates for alkali hydride and alkali hydroxide formation show that excited state chemistry as well as ionization may play a role in laser/flame experiments. In order to sort out the relative roles of excited state ionization and chemistry in alkali seeded flames, experiments are planned to couple the laser to the High Pressure Sampling Mass Spectrometer system for simultaneous mass spectroscopic measurements. By monitoring the influence of laser excitation on both the ionization and alkali hydride/hydroxide formation simultaneously, the role of the excited state atoms in both ionization and chemistry should be determined.

The chemical study of flames and flame inhibitors requires careful measurement of temperature at specific points in the flame and the concentration of species at these points. Because of the chemical kinetics and equilibria involved, the concentrations are related to the temperature by coupled exponential expressions. Consequently very accurate temperature measurements are required. Two spectroscopic methods are being studied: sodium D-line reversal and hydroxyl radical, OH, concentration by absorption. The hydroxyl radical method requires use of the oscillator strength for OH, a commonly used value from the literature. This value has been found to be in error due to omission of vibration-rotation interaction leading to an error by as much as 25 percent in OH concentration. This correction will be useful in future calculations of species concentrations.

Many of our flame studies involve a flame boundary. This may be between clean flame and doped flame or shielding gas (N_2 or Ar) and flame. A major effort went into determining boundary layer effects. The boundary layer region has a large concentration gradient because of reaction of species with greatly different concentrations on either side of the layer. As a consequence of this, different methods of line-of-sight temperature measurement give different results. These differences have been reconciled and corrections may now be made.

Thermophysical Properties of Solid and Liquid Tungsten: Tungsten is an important commercial material because of its refractory nature which permits its being heated to a very high temperature without damage in an inert atmosphere. The melting point has been estimated to be 3680 K. Because of the difficulty of handling tungsten at such high temperatures, most of the thermodynamic and physical properties, in the region of the melting point, are estimates. An attractive method for determining enthalpies of refractory, electrically conducting materials utilizes high frequency levitation and heating. For a dense material like tungsten this could present problems which may be more readily solved by conducting the experiments in space. NASA's program for Materials Processing in Space includes research to test process concepts on the ground that may be carried out in space. Such ground experiments conceivably could turn out to be sufficient. As a result a joint effort has been undertaken by NBS, Rice University, and the General Electric Company Advanced Applications Laboratory to measure tungsten enthalpies by this method, levitation calorimetry. Although the experiment is conducted physically at the GE installation, NBS has been asked to participate in the design and conduction of the experiments.

During the past year the calorimetric system has been made fully operational to design specifications, the major problems in the pyrometric measurement of sample temperature have been isolated, and these methodologies are now considered adequate to the task. The levitation capability problem has become the remaining serious obstacle.

Solid-State Transport and Stability
Subtask 2 of Task 12112

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The Solid State Transport and Stability subtask is concerned with the general area of ionic mobility in ceramic and other ionic solids. The emphasis is on understanding the underlying processes and developing techniques for identifying and studying them and for monitoring materials performance in service. Experimental tools include not only ionic conductivity, but also other means of observing the position and motion of ions in crystals, such as dielectric relaxation, electron spin resonance, and anelastic relaxation.

Current focus is on solid electrolytes, with attention to two important aspects. One is the nature of the charge transport process itself, in the crystal lattice and across interfaces such as the grain boundaries and at the electrode-electrolyte interface. It is desirable in practice, for maximum efficiency, to minimize the resistance of a solid electrolyte device, such as a fuel cell or battery, including that arising at the interfaces. Lifetime of the device depends on the stability with respect to processes allowing this resistance to rise in service. At present no good technique exists for separately measuring these various contributions to the resistance, nor are the factors controlling the interface resistance at all understood. The other important aspect concerns directly the long-term stability of solid electrolytes with respect to such processes as defect clustering, order-disorder crystal structure transformations, and dopant-ion drift under steady electric fields. These are processes expected to influence the crystal lattice resistance and therefore to contribute to degradation of the desirable properties in service. Data on these changes and their rates in the fluorite-structure oxides are needed in assessing the potential of these materials as electrolytes in fuel cells and other devices.

The work is of direct interest to several industry groups using solid electrolytes in their products and processes. The technologies involved include fuel cells for utility power generation and transportation motive power; high energy density batteries for transportation applications; gas sampling probes for industrial and automobile process monitoring and control, and for air pollution monitoring; and research instrumentation for gas composition control and measurement. In this regard, we are participating in the National Fuel Cell Program jointly operated by the Department of Energy and the Electric Power Research Institute. In a more indirect fashion, the techniques we are investigating for grain boundary studies may be useful in following the kinetics of sintering and grain growth in general, and as such should have wide application to the ceramic industry. They should also yield information concerning electron-hole recombination effects at grain boundaries in semiconductors, and may prove useful in that industry also. Finally, the work is directed toward identifying the basic atomistic processes governing the ionic transport in the lattice and across grain boundaries and interfaces, in terms of defect models and the influence of impurities and defect clustering and ordering. The models and techniques developed are expected to further the science of ionic conduction and mass transport in ceramics in a more general way.

The list of materials under study has expanded during this past year. We continue to be concerned with grain-boundary and order-disorder effects in Y-doped CeO_2, and related fluorite-structure oxygen-ion conductors such as stablized ZrO_2. We are also studying Sr-doped $LaCrO_3$ and $YCrO_3$, ceramics which exhibit mixed ionic/electronic conduction, depending on dopant concentration, and which may find application as high-temperature electronic conductors in fuel cells and MHD channels. Finally, we have found in polyacetylene, a conducting polymer, an interesting material upon which to test ways to extract information about interfacial transport processes from the frequency dispersion of the impedance. We are collaborating with Dr. R. A. Snellgrove of the General Refractories Company in the work on $LaCrO_3$, and are indebted to him for the materials. We also gratefully acknowledge the provision of $YCrO_3$ samples by Dr. T. Negas and Mr. W. Hosler of Division 565, the provision of magnesium-stabilzed ZrO_2 specimens quenched from both the solid-solution and the precipitation regions of the phase diagram by Professor Arthur Heuer of Case Western Reserve University, and of polyacetylene samples by Professor A. Heeger of the University of Pennsylvania.

Nature of the Charge Transport Process: The dispersion of the impedance of polycrystalline conductors (with respect to the frequency of the measuring signal) contains information about charge transport in the interior of the grains, at grain boundaries and other inhomogeneities, and at the interfaces with electrodes. A major theme of the current work is to learn how to extract this information from the data on the frequency dependence of the impedance. In previous work we developed an equivalent circuit to describe the impedance data for Y-doped CeO_2 ceramics over the frequency range from about 50 Hz to about 13 MHz. A major problem encountered with this approach is that one must select *a priori* the model to fit, and it is not always clear what the correct model is. Figure 1, for instance, shows the results of attempts to fit our standard equivalent circuit, shown as an inset in the figure, to data on Y-doped CeO_2. The grain boundary impedance Z_{gb} was represented by a Cole-Cole distribution of time constants (K. S. Cole and R. H. Cole, J. Chem. Phys. 9, 341 [1941]), and the electrode impedance Z_{el} by a simple linear law

$$Z_{el} = A/(j\omega\tau)^n$$

where A, τ, and n are adjustable parameters, n lying between 0 and 1, $j = \sqrt{-1}$, and ω is the circular frequency. The discrepancy between calculated and observed points in figure 1 is persistent and not a result of fitting errors. It makes convergence of the least-squares computer fitting routine very difficult. It seems probable that it arises from the choice of the Cole-Cole distribution, and we plan to explore other distributions in the future. In order to understand how the details of these distributions influence the impedance data, we have also been exploring the impedance values calculated on the basis of model equivalent circuits using various distributions, for comparison to actual data.

It appears possible, with our rather wide range of frequencies, to perform an analysis that is considerably less model-dependent. This technique, described with reference to dielectric measurements by Misell and Sheppard (J. Phys. D: Appl. Phys. 6, 379 [1973]), treats the impedance as arising from a series array of parallel R-C circuits with an unknown distribution of time constants. By suitable mathematical deconvolution techniques this distribution of time constants can be obtained from the frequency dependence of either the real or the imaginary part of the impedance. With our computer-controlled data-gathering facility it is quite feasible to obtain data at 100 or more frequencies distributed evenly in log frequency space, very much facilitating the computations. Successful transformations of this kind have been obtained, but the resolution is not yet satisfactory, and work in the future will be aimed at improving it.

Previous work revealed important differences in the component of the impedance ascribed to the grain boundaries in specimens of Y-doped CeO_2 prepared in rather different ways. Current work is continuing with studies of the influence of specimen annealing on this component. We hope also to enlist the aid of the new STEM being installed in Division in searching for compositional and structural differences. We have also obtained (courtesy of Dr. Roy Rice, Naval Research Laboratory) a number of large specimens of Y-doped ZrO_2, with properties similar (but not identical) to the Y-doped CeO_2, containing only a few large crystallites and grain boundaries. We hope to do direct and fundamental experiments on these grain boundaries to correlate changes in impedance with changes in the grain boundaries.

Inhomogeneities other than grain-boundaries can also contribute to the impedance. Magnesium-stabilized zirconia, ZrO_2 containing about eight mole percent MgO, is metastable in the highly oxygen-conducting fluorite phase below about 1700 °C. We have compared the impedance of otherwise identical specimens annealed (1) above this temperature, in the single-phase fluorite-structure solid solution region of the phase diagram, and (2) below, in the two-phase region in which we expect precipitation of tetragonal-structure ZrO_2 particles in an MgO-rich matrix. We find that the precipitation anneal does result in the appearance of an additional contribution to the impedance, as shown in figure 2. In this figure, the additional contribution is shown in the inset, and has all the appearance of a series distribution of parallel R-C networks with a somewhat broadened distribution of time constants.

The impedance can also reveal information about the electrode/electrolyte interface. This interface for Sr-doped $LaCrO_3$ ceramic with sputtered Au or Pt electrodes has shown a strong, and surprising, sensitivity to the oxygen activity at low temperatures, down at least to the neighborhood of room temperature. Figure 3 shows this dependence at 52 °C. When a specimen previously equilibrated with O_2 at one atmosphere (0.1 MPa) pressure was exposed to tank N_2 ($PO_2 \sim 10^{-5}$ MPa) an increase occurred in the contact resistance by almost two orders of magnitude. This change in resistance was reversible, the resistance changing back to its lower value when the N_2 was replaced by O_2. These changes appear to be compatible with a model in which compensation for the dopant Sr ions in the surface is primarily by oxygen vacancies whereas in the bulk it is primarily by electronic holes, and the oxygen vacancy concentration (state of reduction) follows the atmospheric oxygen activity by a diffusion process. Since only a thin surface layer (we estimate about 10^{-7} m) is involved, the chemical diffusion coefficient for oxygen is not hopelessly large ($\sim 10^{-16}$ cm^2/sec). Similar effects have been seen in the grain boundary impedance of Ca-doped $YCrO_3$, and this difference in behavior between the surface, both intergranular and exterior, and the grain interior may be a general feature of these perovskite-structure chromites.

Polyacetylene is a polymer film representing a very different structure. There are no "grains" and "grain boundaries" as such, but instead there are fibers or crystalline regions composed of bundles of polymer chains, along which electronic charge carriers can move with relative ease. The transport of charge from one chain to another, and even more from one fiber to another, must represent a more difficult process, so that interchain or interfiber contacts may be expected to behave electrically like grain boundaries in ceramics. We find indeed that the impedance reflects the presence of such electrical barriers or inhomogeneities. We find, furthermore, that doping of the polymer with oxygen has a strong effect on the intrinsic, interchain resistivity, no effect on the geometric capacitance, and only a small effect, if any at all, on the inhomogeneity impedance. This is satisfying, since it accords with the generally accepted notion that doping of polyacetylene affects primarily the number of charge carriers. The fact that the doping qualitatively affects the electrode resistance and capacitance as one would expect for changes in charge carrier concentration at a barrier arising from some sort of depletion layer is also in accord with this view of the doping process.

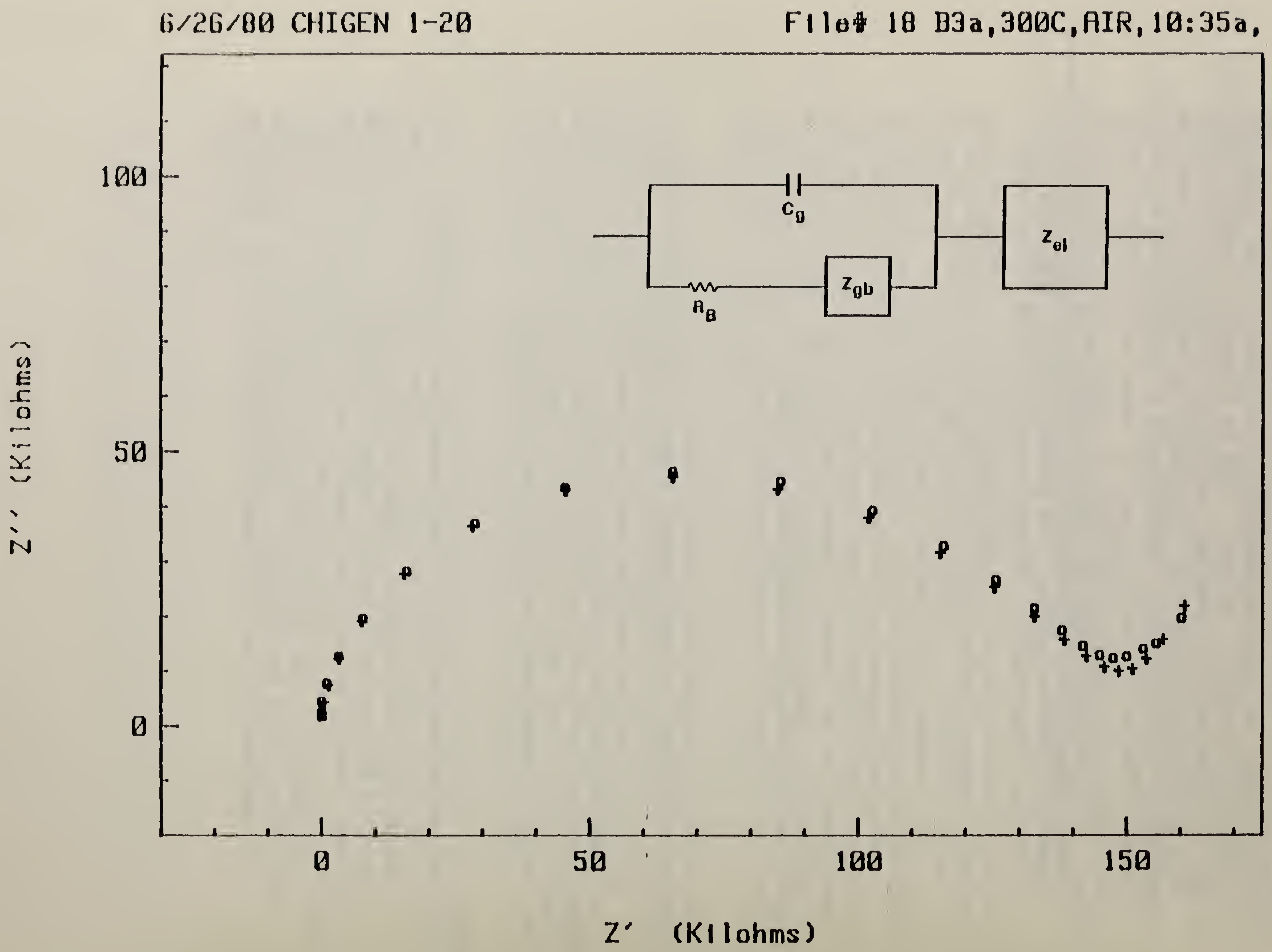
Long-Term Stability of Solid Electrolytes: The basic transport process in ionic conductors is carried on by lattice defects, oxygen vacancies in the case of the doped CeO_2 we are studying. In materials whose conductivity is high enough to be of technological interest, the dopant ion and vacancy concentrations are so high that association among these defects plays a major role in determining the transport properties. This aspect of our work is concerned with elucidating these associations and their interactions with the transport process. We are approaching this problem from both ends of the concentration range, the high end where association will lead to ordered phases and order-disorder transformations, and the low where discrete clusters or complexes of a few defects can be detected.

The stimulation of an order-disorder transformation can be done by long-time anneals, over a range of temperatures and compositions to map the effect on the phase diagram. The furnaces and controls for such long-term anneals have been completed, and some, but not all, of the specimens prepared for a study of the effect of long-term (at least 32 weeks at temperature) anneals on the intrinsic and grain-boundary impedance of Y-doped and Gd-doped CeO_2 as a function of the cation ratio of dopant to Ce (values of 10/90, 20/80, and 30/70 have been chosen for study) and as a function of temperature (from about 500 °C to about 1200 °C).

The preparation of materials worthy of study has occupied considerable time. A technique of homogeneous precipitation has been worked out for preparing mixed oxide powders of R_2O_3 and CeO_2, where R = yttrium or a rare earth. With the resulting powders, ceramics over 95-97 percent dense have been prepared by thermal sintering, and over 99.5 percent dense by hot pressing. These ceramics exhibited very sharp x-ray diffraction patterns and quite narrow distributions of grain size. Specimens containing Y at the 10/90 composition are available. A commercial laboratory is preparing the others (Y at 20/80 and 30/70, Gd at 10/90 and 20/80), and has prepared the powders but has not completed the hot-pressing.

In order to assay the compositions in terms of major components, x-ray fluorescence will be used. Work on preparing standards (dissolved in $Li_2B_4O_7$ glass) for comparison containing variable concentrations of Y with a fixed concentration of Ce has shown a precision of about one percent in the Y/Ce ratio. Standards are also being made with variable Ce and fixed Y.

A preliminary annealing study has been started at 1000 °C, using Y-doped CeO_2 at the 10/90 and 30/70 ratios prepared by thermally sintering chemically prepared powders. The effects noted of the annealing on the electrical properties will be used in designing the fuller study.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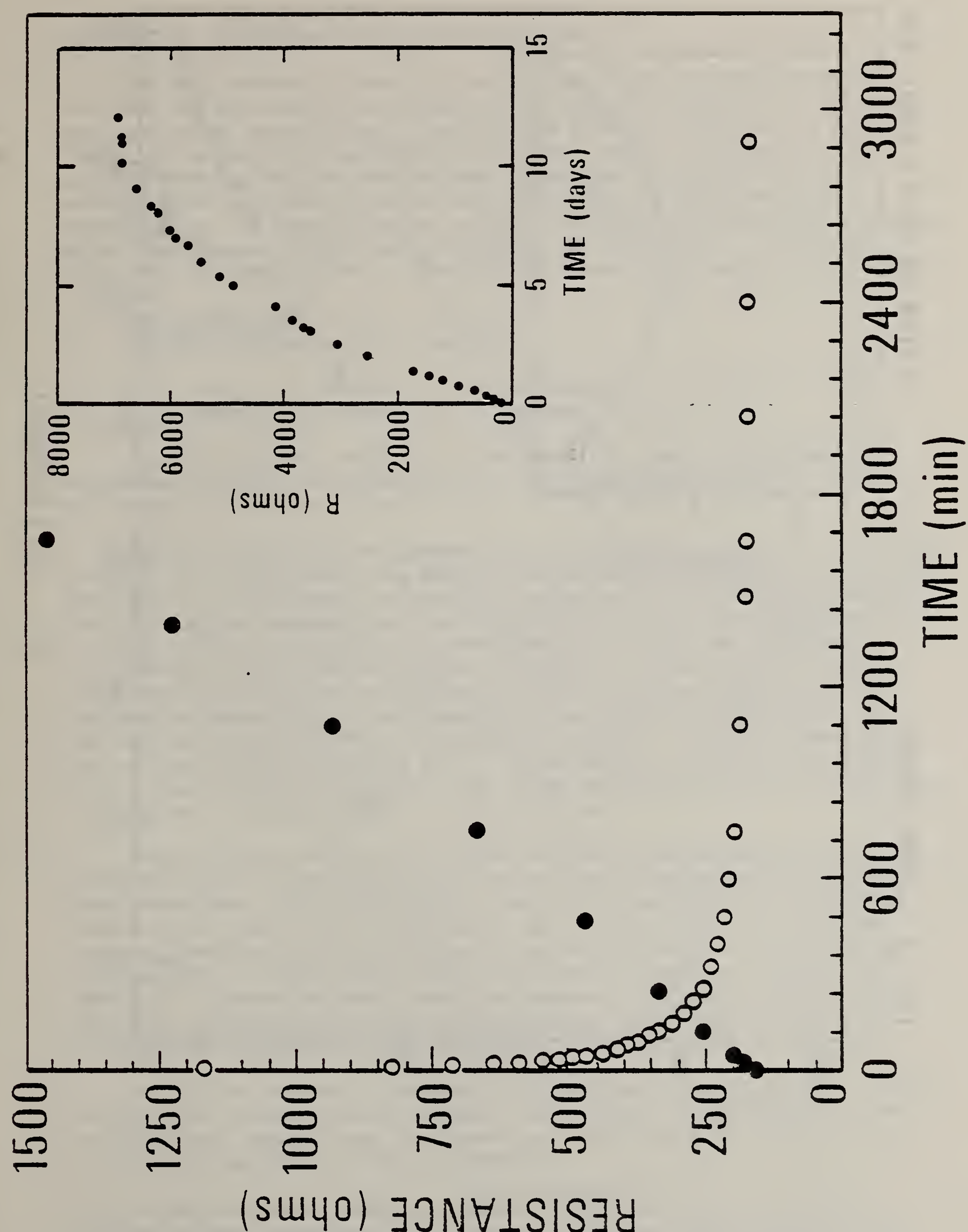

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1000
750
500
250
0
0
600
1200
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2400
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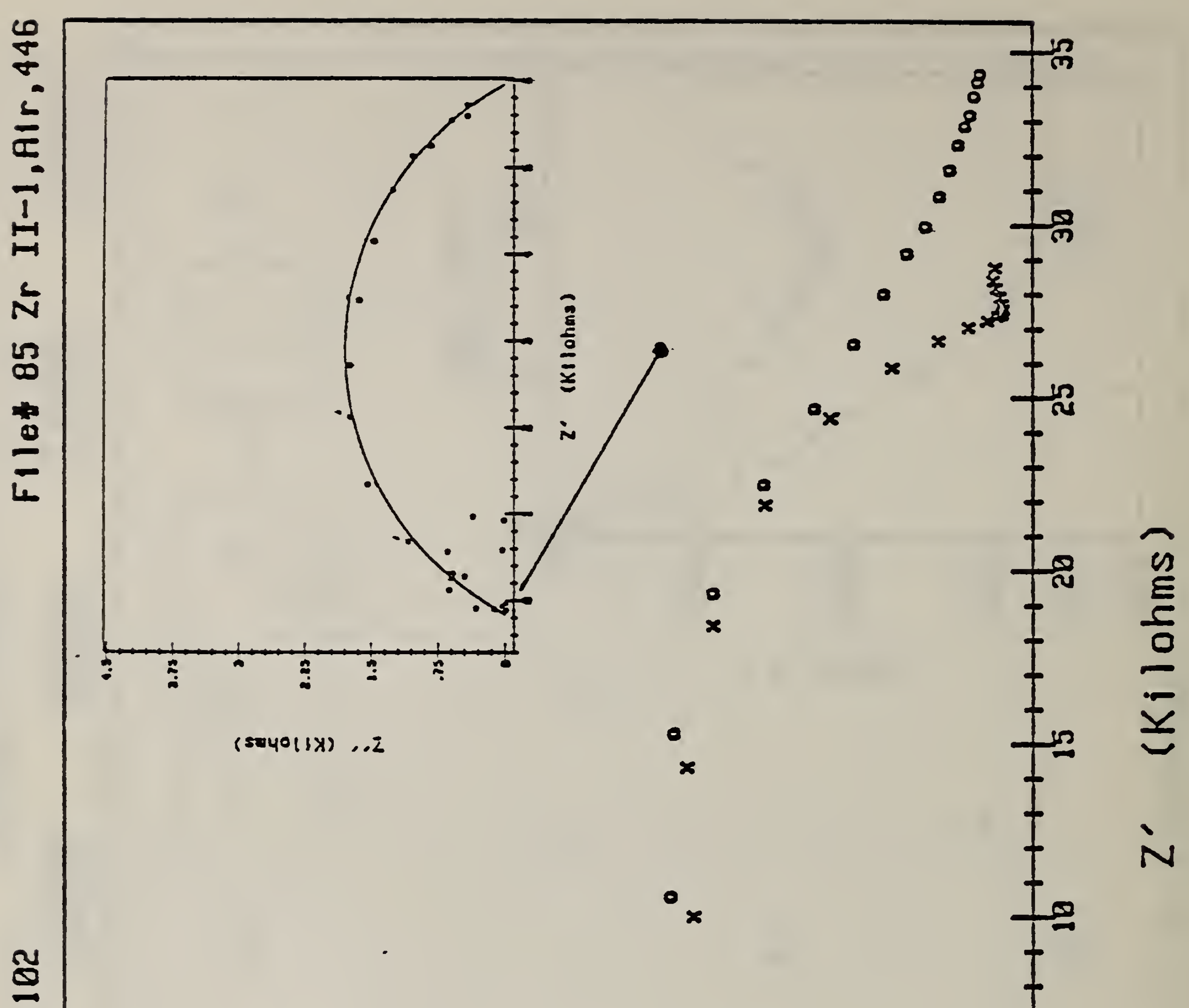
TIME (min)
R (ohms)
8000
6000
4000
2000
0
0
5
10
15
TIME (days)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Z' (Kilohms)

RECYCLED OIL PROGRAM--Division 561 Activities

The Tribochemistry Group of the Chemical Stability and Corrosion Division has the special assignment of providing a tecnical base of data and measurement methodology to support the Bureau's Recycled Oil Program (ROP). This program is mandated by Congress, under the Energy Policy and Conservation Act, to provide test procedures which can be used to establish the substantial equivalency of virgin and recycled oils. Additionally, the Group provides, within the Center for Materials Science, major competences in the chemical aspects of lubrication, friction, wear, and characterization of complex hydrocarbons including lubricants.

<u>Tribochemistry</u>
Subtask of Recycled Oil Program

S. M. Hsu, J. J. Comeford, A. L. Cummings, H. J. Brown P. T. Pei, S. J. Weeks, R. S. Gates, D. E. Mathews, C. S. Ku

Current technical effort is directed mainly toward development of measurement methods and standards for re-refined lubricating oils used as automotive crankcase oils.

The most important requirement for assuring the quality of re-refined motor oil is development of a set of test procedures capable of monitoring the quality, consistency, and additive response of the basestock between periodic engine sequence test qualifications. These test procedures are crucial in order to accomodate re-refined oils within the existing API-SAE-ASTM classification system. (Note: API = American Institute; SAE = Society of Automotive Engineers; ASTM = American Society for Testing and Materials). Development and evaluation of these tests by NBS are particularly difficult because no such set of test procedures exists for virgin lubricating oils. Historically, virgin oil producers were instead required to control the crude source and refining technology. This option is not applicable to oil recyclers.

There has been sufficient engine testing on re-refined oils to establish that: (1) a high quality re-refined lubricating oil which has been formulated with a high quality additive package can be comparable to a virgin oil similarly formulated, and (2) that both will provide adequate performance in most types of automotive service. The problem which exists at the present time is the lack of technical information and data to determine which tests are necessary and how often they should be applied in order to assure that the re-refined oil basestock is consistent between the engine tests.

At NBS the program is underway in this Group to evaluate the chemical and physical test procedures used on lubricating oil basestocks, as well as to perform research and development on bench-scale performance tests to establish basestock additive response.

Accomplishments last year include the evaluation of six physical properties test procedures, four chemical property test procedures, and five test procedures in the performance area. We have also initiated the ASTM/NBS basestock consistency program to examine the consistency of basestocks produced commercially. Important experimental competences in wear, hydrocarbon separation, and characterization have been established through equipment procurement and staffing.

There are six projects: physical properties, chemical properties, hydrocarbon separation, oxidation stability and deposit simulation, friction and wear, and NBS/ASTM Basestock consistency study. These projects are described below.

Physical Properties: The main objective in this area has been to establish a laboratory capable of producing data on all typical physical properties necessary for the characterization of lubricating basestocks and other petroleum products. The physical property methods, most of which are ASTM methods, were evaluated with particular emphasis on their applicability to re-refined basestocks. Seven re-refined base oils were purchased from various re-refiners throughout the country in ten drum lots. After detailed characterization, these oils could serve as reference materials for testing by various organizations and laboratories. Data on a selected set of virgin basestocks were accumulated for comparison. The test methods used are: kinematic viscosity at 40 °C and 100 °C, low temperature viscosity at -18 °C, viscosity index, color, pour point, API gravity, density at 20 °C, refractive index, and flash point. Establishment of this data base on virgin and re-refined base stocks allows the use of correlation programs to help characterize their quality. The simulated boiling point distribution by gas chromatography method is currently being evaluated.

The physical properties laboratory has been utilized by the Office of Standard Reference Materials (OSRM) to measure sulfur in residual fuel oil SRM's. The instrumentation has also been used in conjunction with projects in the Center for Analytical Chemistry (CAC) and the Center for Mechanical Engineering and Process Technology (CMEPT) of NEL.

Chemical Properties: Evaluation of chemical test methods for characterization using a set of reference re-refined and virgin basestocks is underway. Seven test methods were studied. These include ash, sulfur, water, total acid number, nitrogen, basic nitrogen, and carbon residue. Some of these are highlighted below.

Ash: Ash content of an oil refers to the metal content of an oil after combustion. Some metals such as lead and magnesium can be lost during the combustion process due to the low boiling points of their oxides. Sulfuric acid can be added to convert the oxide to sulfates. This is then called the sulfated ash. Three ashing methods, ASTM D482 ("regular"), D874 (sulfated), and wet ashing were investigated. The utility of the methods as a simple means for monitoring residual metal content of base oils has been established and a modification of ASTM method D874 developed, extending the lower range of applicability of the method. For the reference group of 17 basestocks run in triplicate, the sulfated ash for the ten re-refined base stocks ranged from 0.0005 to 0.018 percent with a mean value of 0.0056 percent. The seven virgin basestocks in the group ranged from 0.0000 to 0.0038 percent with a mean value of 0.0007 percent. The ash values for the re-refined stocks in general were significantly higher than for the virgin stocks. This corresponded to significantly higher metal contents for the re-refined stocks as determined by atomic absorption and atomic emission spectrometry.

Degree of metal retention during ashing was determined for the three methods by adding known amounts of metals to metal free oils, ashing the sample, dissolving the ash and analysis by atomic absorption spectrometry. Single element additions for Mg and Pb were done for each method and five element additions for two levels of metal were completed. Ca, Fe, and Zn recoveries were essentially 100 percent for all ashing methods. Retention of Mg and Pb was 80 percent for wet ashing and 80 and 50 percent, respectively, for the sulfated ash. Lead recovery was quite poor for the regular ash (30 percent).

Water Content: Water content in a relatively pure oil is limited by the solubility water in oil. In re-refined oils, there is a potential contamination of residual dispersant/detergent molecules which could increase the amount of water solubilized in oil drastically. Water content in base oils is undesirable with respect to corrosion.

In order to establish a procedure by which water in base oils could be accurately and efficiently determined, we considered several methods. Variations of the Karl Fischer Titration Method were identified as the best candidates for our purposes. We have begun critical experimental evaluation of the sensitivity, accuracy and reproducibility of some of these methods. So far we have evaluated effects of solvents and oils on the reproducibility and analysis time of direct Karl Fischer Titrations. In addition, we have compared three potential water standards, determined the moisture content of seven virgin and ten re-refined base oils by direct titration and begun preliminary tests of an azeotropic distillation method.

Total Acid Number/Total Base Number: Of all of the complex constituants in a lubricating oil, acidic and basic properties are considered to be important. The acid number indicates the amount of acidic species in an oil which could be detrimental to performance by causing corrosion.

The ASTM methods for the determination of these acidic and basic compounds are ASTM D-664 and D-2896. Both are potentiometric titration methods. D-664 is proposed for both TAN (Total Acid Number) and TBN (Total Base Number). D-2896 is proposed for TBN only. We found D-664 is applicable to re-refined base oils and D-2896 needs modifications.

The data collected indicate that the TAN of re-refined base oils is much higher than that of virgin base oils.

Basic Nitrogen Content: Lubricating basestocks are complex hydrocarbon mixtures of paraffinic, naphthenic, and aromatic molecules. There are very few "pure" molecules and most molecules exist as mixed types. A small but important fraction of basestocks consist of molecules containing nitrogen, sulfur, and oxygen moieties.

The reaction of acetous $HClO_4$ with base oil samples has been investigated to estimate the amount of nitrogenous bases present in base oils. We combined two published non-aqueous titration methods and have analyzed lubrication base oils (no additives) from 17 sources in triplicate. The results are usually expressed in two ways: (1) the Total Base Number (TBN); (2) the number of micrograms of nitrogen per gram of oil, assuming that the only bases in the oil are monobasic nitrogen compounds. The data indicate that virgin base oils contain about an order of magnitude more basic nitrogen than do re-refined base oils.

Hydrocarbon Separation/Characterization: Lubricating oil basestocks are complex mixtures of several types of hydrocarbons. Their detailed molecular composition, while difficult to elucidate, is critical to their performance. Structural characteristics, for example, may hold the key to some observed but as yet unexplained phenomena, such as the observation that sulfur compounds can increase or decrease base oil additive response depending on the crude source.

This portion of the program is concerned with methodology for separation of base hydrocarbon materials into aromatic, saturate, and polar fractions. Gradient elution liquid chromatography is the method of choice for this separation. The polar fraction separated by this technique is of particular interest, since it comprises the most active molecular species in a lubricating base oil. Detailed analytical information on the polar material can then be obtained with a variety of techniques including high pressure liquid chromatography, gas chromatography, mass spectrometry, nuclear magnetic resonance, and IR and UV spectroscopy.

The clay-gel chromatographic methods in the ASTM procedure (ASTM D-2007) and its modification (Exxon-Baytown Clay-gel method) were both investigated. The amount of sample charge is 10 gm. The saturated and polar fractions were eluted from the columns by n-pentane and acetone-toluene (50/50) by volume, respectively. The aromatic fraction is either determined by the material balance as in ASTM D-2007 or by refluxing the clay-gel column with toluene as in the Exxon-Baytown method. The agreement of the two methods, especially for the aromatic fractions, is excellent. The data indicate that the polar fraction content of re-refined base oils is generally higher than the virgin base oils. The significance of this difference will be examined with various oxidation tests.

We recently acquired a High Performance Liquid Chromatography (HPLC) system consisting of a Preparative unit and Analytical HPLC. Work has started in developing better separation schemes using HPLC.

Techniques employing absorption spectroscopy, both ultraviolet and infrared, are being investigated for the characterization of lubricating oil base stocks. Included are methods for the analysis of hydrocarbon fractions obtained by various separation techniques. A data terminal has been interfaced with the infrared spectrophotometer providing a capability for storage and retrieval of spectrograms as well as software for automated spectral library searches and the generation of spectral libraries for appropriate classes of compounds.

It is anticipated that this system with the development of hydrocarbon and additive spectral libraries will be a vital element in compound identification.

Oxidation Stability and Deposit Simulation: In the area of performance tests for automobile crankcase oils, the industry-accepted tests include the current engine sequence tests (IIC, IIIC, VC, L-38), laboratory truck engine tests (1H2, LGs, 1D, EMD, T02), full-scale truck engine tests (Mack T-5), fleet tests (Aunt Minnie type, taxi/police fleet heavy duty type, commuter type, tire-track, and EPA cycle type). The expenses involved in running these tests are enormous. There are no commonly accepted chemical/physical laboratory bench tests for indicating in-service performance.

The performance requirements of an automobile crankcase oil are rust protection, corrosion resistance, low temperature dispersancy (to prevent sludge formation), detergency (to keep engine parts clean), solvancy (to solubilize oxidized products), high temperature stability (to keep piston rings from sticking), viscosity-temperature characteristics (to maintain hydrodynamic lubrication), anti-wear properties, and low frictional resistance. In addition, the oxidation stability of the oil is common to most of these requirements. Laboratory equipment and test procedures for these various performance requirements are numerous (over 100 variations of equipment and test procedures for measurement of friction and wear are contained in a single ASLE publication).

The program plan of the performance testing areas will make use of ASTM Reference Oils as a tool to screen promising procedures. The reference oils are currently being used to monitor all the certified engine test stands in the various testing laboratories all over the United States and in some foreign countries. Some of these Reference Oils even have fleet test data available. These oils can be classified into good, bad, and borderline performance oils. By using these Reference Oils, test procedures can be screened for correlation with in-service performance.

The accomplishment in this area has been the completion of a specialized oxidation laboratory facility. Work has started on the test development of oil oxidation mechanism and simulation. Two procedures were used: the Rotary Bomb Oxidation Test (RBOT) and Oil Thickening Test (OTT).

The Rotary Bomb Oxidation Test (ASTM D-2272) has long been used in industry to screen antioxidants. A total of 10 re-refined oils and seven virgin base oils were tested at standard ASTM conditions of 150 °C in the presence of the copper metal catalyst and water. No chemical additives were used in the tests. The results suggest that the re-refined base oils generally have better stability than the virgin base oils. The repeatability of the test is ± 10 percent.

The standard test procedure provides an easy and quick method to obtain information on the oxidation stability of base oils. However, the use of water and copper catalyst in the test do not reflect the engine in-service conditions. Preliminary studies on additive responses of several oils were also conducted. Results indicate that at higher antioxidant concentration (zinc dithiophosphate) the additive response (oxidation stability improvement) of re-refined base oil appears to be better than that of virgin base oils. Other additive systems will be used to examine the additive response question further.

Preliminary OTT data on a 10W-40 commercial oil were collected. Experiments were run at 175 °C, a gas flow rate of 60 cm^3/min, and with catalysts such as iron powder, copper powder, ferric naphthenate, and NO_2.

Results suggest that within a batch, repeatability is good, but the batch-to-batch repeatability needs further study for improvement. In general, the soluble catalyst (ferric naphthenate) causes more oil thickening than the solid catalyst (iron powder and copper powder).

Friction and Wear: The emphasis in this area is on the chemical aspects of friction and wear. For re-refined base oils derived from many sources of used oils, potential contamination by cutting oil additives, and metal-forming oils could have a significant effect on friction and wear characteristics of the final product.

A laboratory module has been specially equipped to accommodate three wear test apparatus: ring-on-block, four-ball, and pin-and-v. A new four-ball wear tester was specially designed to increase its load, speed range, and ease of wear debris collection and analysis. We have also acquired the Motor Industry Research Association (MIRA) Cam and lifter wear tester which employs the actual cams and lifter parts of an engine. This is the first of its kind in the United States.

The objective in this area is to evaluate various laboratory wear test procedures with respect to their ability to measure the wear performance of lubricating oils. Laboratory bench tests have long been a popular method of evaluating an oil's ability to lubricate because they are more repeatable, far less expensive, easier to run and more sensitive to chemical effects than full-scale engine or fleet tests.

The bench test procedures were evaluated using a set of five ASTM IIID Engine Sequence Test Reference Oils. These Reference Oils have a significant data base and have shown a correlation to actual field performance. The wear data obtained from the engine sequence tests shown in table 1 indicate that the oils can be roughly classified as high or low wear oils. Slow sliding tests performed on a Falex Four-Ball wear tester failed to show any significant difference in wear performance between the reference oils. The anti-wear additives in an oil also function as antioxidants; therefore, an attempt was made to observe the effect of oxidation on wear performance. Reference oils, which are oxidized under identical conditions and run in identical wear tests, showed different responses to wear as shown in table 1. The interesting feature of this is that the high wear reference oils have a greater increase in wear because of oxidation than the low wear reference oils.

An attempt is currently being made to increase the severity of the oxidation to see if the trend of separation between the high and low wear reference oils can be enhanced.

A series of load capacity seizure tests run on the Falex Four-Ball wear tester have a good correlation to the engine sequence test results. The high wear reference oils seize at below 180 kg while all three of the low wear reference oils were able to take loads of above 180 kg before seizure occurred.

A new research quality Roxana Four-Ball wear test machine was received in the spring of 1980, and initial testing on the effect of base stock impurities on wear has begun.

Table 1

Test Results

	Reference Oils				
Test Description	76-A	75B-1	79A	77B-1	77C
Sequence IIID Engine Wear Test					
Cam + Lifter Wear, cm x 10^{-4}	48	46	48	287	277
Wear Classification	Low	Low	Low	High	High
4-Ball Wear Test					
Slow sliding Test[1] Wear Scar diameter, cm x 10^{-3} w/o oxidation	31	33	33	31	29
Wear Scar diameter[1], cm x 10^{-3} w/oxidation[2]	36	35	37	40	37
Step-loading Siezure Test[3]					
seizure load, kg	200	227	218	154	127

[1]Test Conditions: 22.7 kg load, 75 °C, 60 minutes, 200 rpm.
[2]Oil oxidized for 48 hours at 177 °C with used oil as catalyst.
[3]Test Conditions: 75 °C, 200 rpm.

ASTM/NBS Basestock Consistency Study: In conjunction with ASTM, we are jointly sponsoring a study to collect information and data to determine which tests are necessary and how often they should be applied in order to assure that the re-refined basestock is consistent between the engine tests.

The user industries are concerned about the potential lack of consistency of re-refined oil products, and about the potential effects of unusual or unknown contaminants in the used oil feedstock to re-refineries. These potential problems are of particular concern when warranty questions are involved.

In this one-year study, four virgin oil producers and six re-refined oil producers are submitting monthly samples for analysis by a group of 12 organizations, including NBS (Table 2a). These laboratories will analyze the coded samples using over 40 different chemical, physical, and performance tests. The program has been underway since March, 1980.

It is expected that the results from this study will provide much of the data necessary to indicate an appropriate set of test procedures to monitor re-refined basestock consistency.

Table 2

Organizations Cooperating in the ASTM/NBS Basestock Consistency Study and the Tests

Organizations

Bartlesville Energy Technology Center	National Bureau of Standards
Chevron, USA	National Research Council of Canada
Gulf R&D	Suntech, Inc.
Lubrizol	Texaco
Mobil Oil Corporation	U.S. Army MERADCOM

Tests

Physical Property Tests

Demulsibility	Viscosity at 40 and 100 °C
Filterability	Viscosity Index
Gravity	Refractive Index
Color	Pour Point
Cold Cranking Simulator 0 to -40 °C	Carbon Residue
Mini-rotary Viscosity 10 to -40 °C	Boiling Point Distribution
Brookfield Viscosity 0, -20, -40 °C	Foam

Chemical Property Tests

Total Acid Number	Halogens
Saponification Number Nitrogen, Sulfur	Differential Infrared Sunlight Stability
Hydrocarbon Type by Mass Spect.*	Additive Compatibility
Hydrocarbon Type by Liquid Chromatography	Glycol Content
Emission Spectrograph	

Bench Tests

Additive response to oxidation*	Seq III C Simulator
Additive response to wear*	For Anti-oxidant Response Differential Scanning Calorimetry
Rusting	RBOT (Basestock + Additive)
LUBTOT	Turbine Oil Oxidation*

*On selected samples

Other Activities of the Chemical Stability and Corrosion Division

Invited Talks

Ultra-Black Coating for Optical and Solar Devices
Optical Society of America, Rochester, New York
C. E. Johnson
September 9, 1979

Studies of Passive Film Breakdown by Detection and Analysis of Electrochemical Noise
International Conference on Non Traditional Approaches to Study Solid-Electrolyte Interfaces, Snowmass, Colorado
U. Bertocci
September 27, 1979

Possible Applications of Non Traditional Techniques (Solid-Electrolyte Interface) to Technological Problems
International Conference on Non Traditional Approaches to Study Solid-Electrolyte Interfaces, Snowmass, Colorado
J. Kruger
September 27, 1979

Some Aspects of Chemical and Biodegradation of Materials
Thiokol Corporation, Ventron Division, Beverly, Massachusetts
T. D. Coyle
October 5, 1979

Current Progress in the Determination and Speciation of Trace Organometals by HPLC
Washington Chromotography Discussion Group, Gaithersburg, Maryland
F. E. Brinckman
October 18, 1979

Some Issues Affecting Corrosion Protection
Naval Ship Research and Development Center, Annapolis Colloquium, Annapolis, Maryland
J. Kruger
October 19, 1979

The Four-Ball Wear Test for Engine Oil Evaluation
Joint Conference on Measurements and Standards for Recycled Oil/Systems Performance and Durability, NBS, Gaithersburg, Maryland
R. S. Gates
October 24, 1979

Characterization of Lubricating Basestocks
Joint Conference on Measurements and Standards for Recycled Oil/Systems Performance and Durability, NBS, Gaithersburg, Maryland
S. M. Hsu
October 24, 1979

Engine Oil Evaluation Through Bench Testing
Joint Conference on Measurements and Standards for Recycled Oil/Systems Performance and Durability, NBS, Gaithersburg, Maryland
S. M. Hsu
October 25, 1979

Unique Surface Morphology with Extremely High Light Absorption Capacity
Electroless Nickel Conference, Cincinnati, Ohio
C. E. Johnson
November 6, 1979

An Overview of the Microbial Corrosion of Underground Metallic Structures
American Society for Testing and Materials Symposium on Underground Corrosion, Williamsburg, Virginia
W. P. Iverson
November 26, 1979

Alkali Vapor Transport Over Coal Minerals and Slags
Materials Research Society Annual Meeting Symposium on Coal: Materials Properties and Conversion, Cambridge, Massachusetts
J. W. Hastie
November 1979

Measuring the Corrosion Rate of Steel in Concrete
Federally Coordinated Program (FCP) Conference on Highway Research and Development, Williamsburg, Virginia
E. Escalante
December 5, 1979

Microbial Activity in Western Coal Mine Spoils
Biochemistry Group, Clinical Center, National Institutes of Health, Bethesda, Maryland
G. J. Olson
December 7, 1979

Modern Approaches Toward Measurement of Corrosion in Practical Environments
Joint Chesapeake Section, American Society of Nondestructive Testing and Baltimore American Society of Metals Meeting, Baltimore, Maryland
J. Kruger
December 17, 1979

Speciation of Organoarsenicals in Oil Shale Process Waters
Health and Environment Division, Department of Energy, Germantown, Maryland
F. E. Brinckman
December 20, 1979

New Approaches in Corrosion Research
Combined Boston sections of NACE (National Association of Corrosion Engineers) and ECS (Electrochemical Society), Boston, Massachusetts
J. Kruger
January 16, 1980

Economic Effects of Metallic Corrosion in the United States (NBS Study)
Texas Instruments Labs, Attleboro, Massachusetts
J. Kruger
January 17, 1980

Current Trends and Prospects in Speciation of Environmentally Important Trace Organometallic Compounds
Lawrence Berkeley Laboratory, Berkeley, California
F. E. Brinckman
January 24, 1980

Studies of the Propagation of Transgranular Stress-Corrosion Cracks in FCC Alloys
Metallurgy Department Seminar, University of Connecticut, Storrs, Connecticut
E. N. Pugh
February 13, 1980

Chemistry and Flame Retardancy
Northern West Virginia Section, American Chemical Society
Morgantown, West Virginia
T. D. Coyle
March 3, 1980

Chemistry and Flame Retardancy
Kanawha Valley Section, American Chemical Society
South Charleston, West Virginia
T. D. Coyle
March 4, 1980

Chemistry and Corrosion
Central Ohio Valley Section, American Chemical Society
Huntington, West Virginia
T. D. Coyle
March 5, 1980

Chemistry and Corrosion
Western Maryland Section, American Chemical Society
Cumberland, Maryland
T. D. Coyle
March 6, 1980

Thermodynamic and Property Measurements of Liquid Tungsten
NASA--Marshall Space Flight Center
D. W. Bonnell
March 13, 1980

Employment of the Deaf in Science: Barriers and Progress
Gallaudet College Science Day, Gallaudet College, Washington, DC
E. J. Parks
March 18, 1980

Coupling Ferrography with Wear Testing as an Aid to Lubricant Evaluation
Ferrography Workshop, Technical Support Center--Joint Oil Analysis Program, Pensacola, Florida
R. S. Gates
March 19, 1980

Microbial Transformations of Heavy Metals
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico
W. P. Iverson
March 25, 1980

A Review of the National Bureau of Standards Recycled Oil Program
Waste Oil Management Conference, ASLE--Chicago Section and Illinois Institute of Natural Resources, Amoco Research Center, Chicago, Illinois
S. M. Hsu
April 3, 1980

A Review of the ASTM Basestock Consistency Study Plan
Waste Oil Management Conference, ASLE--Chicago Section and Illinois Institute of Natural Resources, Amoco Research Center, Chicago, Illinois
S. M. Hsu
April 3, 1980

Microbial Transformations of Heavy Metals
Microbiology Class, Dr. Norman Gary--Instructor, Hood College, Frederick, Maryland
W. P. Iverson
April 17, 1980

Study of Transport Properties in Polycrystalline Ceramics Using Impedance Measurements
College of Earth and Mineral Sciences, Pennsylvania State University, University Park, Pennsylvania
A. D. Franklin
April 24, 1980

A Review of Laboratory Bench Tests in Assessing the Performance of
Automotive Crankcase Oils
ASLE Annual Meeting, Anaheim, California
S. M. Hsu
May 5, 1980

Re-refined Lubricating Base Oils: Establishing Consistency
and Quality
ASLE Annual Meeting, Anaheim, California
S. M. Hsu
May 6, 1980

Soils and Underground Corrosion
Gas Transmission Conference, American Gas Association,
Salt Lake City, Utah
E. Escalante
May 6, 1980

Simulation of Engine Tests Using Laboratory Bench Tests
Chevron Research Company, Richmond, California
S. M. Hsu
May 9, 1980

Re-refined Lubricating Base Oils: Establishing Consistency
and Quality
API Refining Meeting, Houston, Texas
S. M. Hsu
May 13, 1980

Recent Observations on the Propagation of Stress-Corrosion Cracks
and Their Relevance to Current Models for Stress-Corrosion Cracking
A. R. Troiano Honorary Symposium on Hydrogen Embrittlement and
Stress Corrosion Cracking, Case Western Reserve University,
Cleveland, Ohio
E. N. Pugh
June 3, 1980

New Developments in the Economics and Science of Corrosion
Burgess Memorial Lecture, Washington Chapter-American Society
for Metals, Bethesda, Maryland
J. Kruger
June 4, 1980

Effects of Base Stock Chemical Composition of Friction and Wear
Gordon Research Conference Friction, Lubrication and Wear,
Colby--Sawyer College, New London, New Hampshire
S. M. Hsu
June 9, 1980

Bacterial Corrosion
Gas Operations School
New England Gas Association, Bentley College, Waltham, Massachusetts
W. P. Iverson
June 12, 1980

Biomethylation of Tin
Organotin Environmental Program Association (ORTEPA)
L'Enfant Plaza Hotel, Washington, DC
F. E. Brinckman
June 19, 1980

NBS Program in Chemical Stability and Corrosion Division
Organotin Environmental Program Association (at NBS Gaithersburg)
T. D. Coyle
June 19, 1980

Morphology of Immersion Deposits on Aluminum
American Electroplaters' Society, Atlanta, Georgia
D. S. Lashmore
June 25, 1980

Studies of the Propagation of Stress-Corrosion Cracks
Corrosion Section Seminar, Battelle Columbus Laboratories, Columbus, Ohio
E. N. Pugh
July 14, 1980

Transport Properties by Impedance Measurements for Solid Electrolyte Fuel Cells
National Fuel Cell Seminar, San Diego, California
A. D. Franklin
July 15, 1980

Corrosion
Sagamore Army Materials Research Conference on Surface Treatments for Improved Performance and Properties, Lake George, New York
J. Kruger
July 17, 1980

Molecular Chemistry at High Temperature
IBM, Yorktown Heights, New York
J. W. Hastie
July 22, 1980

Evidence for the Discontinuous Nature of Transgranular Stress-Corrosion Cracking in FCC Alloys
Gordon Research Conference on Corrosion, Colby--Sawyer College, New London, New Hampshire
E. N. Pugh
July 22, 1980

A Qualitative Ellipsometric Approach to Studying Film Growth Under Organic Coatings
Gordon Conference on Corrosion, Colby--Sawyer College, New London, New Hampshire
J. J. Ritter
July 24, 1980

Environmental Organotin Chemistry: Experiences in the Field and Laboratory (Plenary Lecture)
3rd International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin, and Lead; University of Dortmund; Dortmund, West Germany
F. E. Brinckman
July 24, 1980

High Temperature Chemistry of Flames and Slags
Aerodyne Research, Inc., Bedford, Massachusetts
J. W. Hastie
July 25, 1980

Applications of Transpiration Mass Spectrometry
Gordon Research Conference: High Temperature Chemistry
Plymouth, New Hampshire
D. W. Bonnell
August 4, 1980

High Temperature Chemistry of Flames and Slags
General Electric Central Research Laboratory, Schenectady, New York
J. W. Hastie
August 11, 1980

Studies of Hydrogen Embrittlement and Stress-Corrosion Cracking in an Al-Zn-Mg Alloy
3rd International Conference on Effect of Hydrogen on Behavior of Materials, Jackson Lake Lodge, Wyoming
E. N. Pugh
August 28, 1980

Activities of the NBS Chemical Stability and Corrosion Division
International Tin Research Institute, Greenford, England
T. D. Coyle
September 1, 1980

Technical and Professional Committee Memberships

American Chemical Society
Inorganic Chemistry Division--Nonmenclature Committee
T. D. Coyle, Chairman

American Association of Civil Engineers
Committee on Corrosion Protection of Steel Structures
W. F. Gerhold, Member

American Petroleum Institute and American Society for Testing and Materials
Joint Committee on Static Petroleum Measurement, Working Group on Water and Sediment
J. J. Comeford, Member

American Society for Testing and Materials
A05: Metallic Coated Iron and Steel Products
W. F. Gerhold, Chairman, Member:
A05.09: Advisory, Chairman
A05.14: Sheet Tests
A05.15: Wire Tests
A05.16: Hardware Tests, Chairman

B08: Electrodeposited Metallic Coatings and Related Finishes
F. Ogburn, Member:
B08.01: Terminology, Editing Public Relations and Metrication
WG.05: Metrication, Chairman
B08.03: Decorative Copper, Nickel, Chromium, and Nickel-Chromium Coatings
WG: Electrodeposited and Electroless Black Coatings for Solar Use
B08.04: Zinc and Cadmium Coatings
B08.05: Coatings of Tin, Lead, and Their Alloys
B08.06: Anodic and Chemical Conversion Coatings on Aluminum and Magnesium Alloys
B08.08: Engineering Coatings
B08.09: Precious Metal Coatings
B08.10: General Test Methods
WG.01: Measurement of Coating Thickness, Chairman
B08.11: Government Specifications, Chairman
B08.20: Technical Advisory Groups to ISO/TC 107
D. S. Lashmore, Member:
B08.02: Substrate Preparation
B08.03: Decorative Copper, Nickel, Chromium, and Nickel-Chromium Coatings
WG: Electrodeposited and Electroless Black Coatings for Solar Use
B08.08: Engineering Coatings
B08.10: General Test Methods

C5: Manufactured Carbon and Graphite Products
W. S. Horton, Member:
C5.02: Nomenclature, Units, and Editorial Matters, Chairman
C5.05: Nuclear Applications
C5.06: Executive Subcommittee

D2: Petroleum Products and Lubricants
S. M. Hsu, Member:

T-B:	Automotive Lubricants
T-B-II:	Heavy Duty Engine Oils
T-Jt.B/P:	Basestock Characterization
T-P:	Recycled Petroleum
T-P-II:	Used Oils and Basestocks
T-P-III:	Fuel Oils
RDD-II:	Elemental Analysis
RDD-IV:	Flow Properties
RDD-IX:	Oxidation

C. Ku, Member
R. Gates, Member:

T-L:	Industrial Lubricants

J. J. Comeford, Member:

C-I:	Advisory Committee
T-E-I:	Burner Fuel Oils
RDD-IV:	Hydrocarbon Analysis
RDD-IV-F:	Absorption Spectroscopy Methods
T-P:	Recycled Petroleum Products and Lubricants, Advisory, Vice-Chairman
T-P-I:	Automotive Lubricants
T-P-II:	Used Oils and Base Stocks
T-P-III:	Fuel Oils, Chairman
T-P-IV:	Industrial and Hydraulic Oils
T-P-VI:	Miscellaneous Products
T-P-VII:	Editorial
RDD-IX-F:	Used Oils Oxidation-Nitration

A. L. Cummings, Member:

RDD-III-A:	Chemical Methods
RDD-III-C:	Electrometric Method
RDD-VI-A:	Chemical Analysis
RDD-Jt.API/ASTM:	Water and Sediment

P. T. S. Pei, Member:

RDD-III:	Elemental Analysis
RDD-III-A:	Chemical Methods
RDD-IV:	Hydrocarbon Analysis
RDD-IV-A:	Chemical Analysis
RDD-IV-C:	Liquid Phase Chromatography
RDD-VI:	Analysis of Lubricants

S. J. Weeks, Member:

T-P:	Recycled Petroleum Products
RDD-III:	Elemental Analysis
RDD-IV:	Hydrocarbon Analysis
RDD-VII:	Flow Properties

E13: Molecular Spectroscopy

R. B. Johannesen, Member:

E13.07: Nuclear Magnetic Resonance, Chairman

E34: Occupational Health and Safety Aspects of Materials, Physical and Biological Agents

F. E. Brinckman, Member:

E34.10: Definitions and Nomenclature, Co-Chairman

G01: Corrosion of Metals

U. Bertocci, Member:

G01.11: Electrochemical Measurements in Corrosion Testing

E. Escalante, Member:

G01.10: Corrosion in Soils, Chairman

W. F. Gerhold, Member:

G01.01:	Research
G01.04:	Atmoshperic Corrosion
G01.05:	Laboratory Corrosion Tests
G01.06:	Stress Corrosion Cracking and Corrosion Fatigue
G01.98:	Advisory Committee on Exposure Test Facilities

W. P. Iverson, Member:

G01.10: Corrosion in Soils

TG: Electrochemical Polarization Techniques for Measurement of Corrosion Rates in Soils, Chairman

J. Kruger, Member:

G01.02:	Nomenclature
G01.90:	Executive Committee
G01.99:	Standing Committee on Liaison, Chairman

E. N. Pugh, Member:

G01.06:	Stress Corrosion Cracking and Corrosion Fatigue
G01.06.05:	Section on Dynamic Testing, Chairman

Controlled Release Society (International)
Publications Committee
F. E. Brinckman, Member

Carnegie Mellon Institute of Research
Industrial Energy Productivity Project: Materials Trends Group
J. Kruger, Member

Electric Power Research Institute
Corrosion Advisory Committee
J. Kruger, Member

Electrochemical Society
Corrosion Division
J. Kruger, Member, Past Chairman

Editorial Committee
J. Kruger, Member
U. Bertocci, Member

Technical Affairs Committee
J. Kruger, Member

Corrosion Monograph Series Committee
J. Kruger, Member

Federation of Materials Societies
J. Kruger, Member,
Board of Trustees
Long-Range Planning Committee

Gordon Research Conferences
Council
J. Kruger, Member

International Committee for the Characterization and Terminology of Carbon
W. S. Horton, Vice Chairman

International Corrosion Council
J. Kruger, Member & U. S. Delegate

International Standards Organization
TC107: Metallic and Other Non-organic Coatings
F. Ogburn, Delegate:
1: Terminology, Delegate
2: Methods of Inspection and Coordination of Test Methods, Delegate
3: Electrodeposited Coatings and Related Finishes, Delegate
7: Corrosion Tests, Delegate

TC156: Corrosion of Metals
J. Kruger, Delegate:
1: Terminology, Delegate

International Union of Pure and Applied Chemistry

II: Inorganic Chemistry Division

Division Committee

W. S. Horton, Member

Commission II-2: Nomenclature of Inorganic Chemistry

T. D. Coyle, Titular Member, Secretary

Commission II-3: High Temperatures and Refractory Materials

W. S. Horton, Associate Member

Subcommission II-3.1: Characterization and Terminology of Carbon, Co-Chairman

Joint Committee of Atomic and Molecular Physical Data
R. B. Johannesen, Member: NMR Subcommittee

(Jointly Sponsored by the American Chemical Society, American Physical Society, American Society for Mass Spectrometry, American Society for Testing and Materials, Coblentz Society, Manufacturing Chemists Association, Optical Society of America, Society for Applied Spectroscopy, and Spectroscopy of Society of Canada.)

National Association of Corrosion Engineers

International Relations Committee

J. Kruger, Liason Member

Government Affairs Committee

J. Kruger, Liason Member

Publications Committee

J. Kruger, Member

Technical Practices Committee

J. Kruger, Member

Standing Committee on Technology Assessment

J. Kruger, Member

T10: Underground Corrosion Control

E. Escalante, Member

T3: Corrosion Science and Technology

W. P. Iverson, Member

T3L: Electrochemical and Electrical Techniques for Corrosion Measurement and Control

J. Kruger, Member

SC.B: Corrosion Products

National Research Council
    Committee on High Temperature Science and Technology
    J. W. Hastie, Member

National Materials Advisory Board
    Committee on Environmentally Assisted Cracking Test: Methods for High Strength Steel Weldments
    J. Kruger, Member
    E. N. Pugh, Liason Representative

    Committee on the Assessment of the Characterization (in-situ--Downhole) of Geothermal Brines, National Materials Advisory Board
    U. Bertocci, Member

    Committee on Radioactive Waste Management
        Subcommittee on Review of Swedish KBS-2 Plan
        J. Kruger, Member
        U. Bertocci, Consultant

    Committee on Recommendations for U. S. Army Basic Scientific Research
    J. Kruger, Member:
        Corrosion, Surfaces, and Interfaces Section, Chairman

National Science Foundation
    Faculty Research Participation Program
    F. E. Brinckman, Panel Chairman

Offshore Technology Conference
    Executive Committee
    J. Kruger, Member

Surgeon's General Review Panel on Special Surveillance Program for Leaking Weteye Bombs
    J. Kruger, Member

U.S./U.S.S.R. Study Group on Corrosion
    J. Kruger, Member
    Passivity and Electrochemistry Project Coordinator

Publications

Ultra-Black Coating for Optical and Solar Devices--A Summary
C. E. Johnson
J. Optical Society of America, 69, 1400 (October 1979)

Unique Surface Morphology with Extremely High Light Absorption Capacity
C. E. Johnson
Proceedings of Electroless Nickel Conference, Cincinnati, Ohio, Individual Volume (November 1979)

Fundamentals of Corrosion of Metallic Implants
J. Kruger
Corrosion and Degradation of Implants
B. C. Syrett and A. Acharya, Editors, ASTM STP 684, p. 107 (1979)

Stress Corrosion Testing at Elevated Temperatures in Simulated Coal Conversion Gases
G. M. Ugiansky and C. E. Johnson
Proceedings of the 7th International Congress on Metallic Corrosion, ABRACO, Rio de Janeiro, Brazil, p. 915 (1979)

The Role of Noncrystalline Films in Passivation and Breakdown of Passivation
A. G. Revesz and J. Kruger
ibid., p. 330 (1979)

An Electrochemical Study of an Al-Zn-Mg Alloy
G. M. Ugiansky, J. Kruger, and R. W. Staehle
ibid., p. 605 (1979)

Detection and Analysis of Electrochemical Noise for Corrosion Study
U. Bertocci
ibid., p. 2010 (1979)

Application of a Graphite Furnace Atomic Absorption Detector Automatically Coupled to a High Performance Liquid Chromatograph for Speciation of Metal-containing Macromolecules
E. J. Parks, F. E. Brinckman, and W. R. Blair
J. Chromatography, 185 563 (1979)

International Cooperation on Characterization and Terminology of Carbon and Graphite
W. S. Horton
Pure and Appl. Chem., 51, 1561, Pergamon Press, Ltd. (1979)

Spectroscopy and Photophysics of the $CF_2 \tilde{A}\,{}^4B_1$-$\tilde{X}\,{}^4A_1$ System
D. S. King, P. K. Schenck, and J. C. Stephensen
J. Mol. Spec., 78, 1 (1979)

Improved Sensitivity for Laser Enhanced Ionization Spectrometry in Flames by Stepwise Excitation
G. C. Turk, W. G. Mallard, P. K. Schenck, and K. C. Smyth
Analy. Chem., 51, 2408 (December 1979)

Slow Transient Phenomenon in Y-Doped CeO_2
C. K. Chiang, A. L. Dragoo, and A. D. Franklin
Proc. of International Conference on Fast Ion Transport in Solids, Electrodes, and Electrolytes, p. 661, Lake Geneva, Wisconsin (May 21-25, 1979)

Preparation of Pt-Fe Alloy Foils by Electrodeposition of Fe
A. D. Franklin and J. Epp
J. Electrochm. Soc., 126, 2126 (1979)

State of the Art of Electrodeposition on Anodized Aluminum
D. S. Lashmore
Metal Finishing, 78, 21 (1980)

Progress in Plating on Aluminum
D. S. Lashmore
Plating and Surface Finishing, 67, 36 (1980)

A New Ellipsometric-Electrochemical Approach to the Study of Corrosion Under Organic Coatings
J. J. Ritter and J. Kruger
Proceedings of Division of Organic Coatings and Plastics Chemistry, American Chemical Society, San Francisco (1980)

Electroforming a Micrometer Scale of 50 μm (2 mil) Overall Length
J. P. Young, F. Ogburn, and D. B. Ballard
Metal Finishing, 78, 8 (1980)

The Morphology of Immersion Coatings on Aluminum
D. S. Lashmore
Plating and Surface Finishing, 67, 37 (1980)

Thin Zinc Film on Aluminum
D. S. Lashmore
J. Electrochemical Society, 127, 3 (1980)

Mössbauer Spectroscopy of Polycrystalline Steel Fibers
D. S. Lashmore, L. J. Swartzendruber, and L. H. Bennett
Applied Physics Letters, 36, 1 (1980)

A Low-Noise Potentiostat for the Study of Small Amplitude Signals in Electrochemistry
R. W. Shideler and U. Bertocci
J. Res. NBS, 85, 211 (1980)

Thickness of Gold Coatings Measured with a Calibrated SEM
F. Ogburn and D. B. Ballard
Plating and Surface Finishing, 67, 49 (1980)

Black Electroless Nickel Surface Morphologies with Extremely High Light Absorption Capacity
C. E. Johnson
Metal Finishing, 78, 21 (July 1980)

Graphite Furnace Atomic Absorption Spectrophotometers as Automated Element-specific Detector for High Pressure Liquid Chromatograph (HPLC), the Determination of Arsenite, Arsenate, Methylarsonic Acid, and Dimethylarsinic Acid
F. E. Brinckman, K. L. Jewett, W. P. Iverson, K. J. Irgolic, K. C. Ehrhardt, and R. A. Stockton
J. Chromatography, 191, 31-46 (1980)

What Really Does Happen to Electronically Excited Atoms in Flames
K. C. Smyth, P. K. Schenck, and W. Gary Mallard
Amer. Chem. Soc. Symp. Series, 134 (1980)

Internal Friction and Sodium Transport in Beta Alumina
J. H. Simmons, A. D. Franklin, K. F. Young, and M. Linzer
J. Am. Ceram. Soc., 63, 78 (1980)

Underground Corrosion
E. Escalante
Corrosion and the Building Industry, Building Science Series (NBS BSS)
in press

A Field Study on the Corrosion of Concentric Neutral Cable
E. Escalante, U. Bertocci, and J. L. Mullen
Materials Performance
in press

The Location Effect on the Corrosion of Steel in Stagnant Solutions
S. Wolynec and E. Escalante
Corrosion Science
in press

Determination of True Polarization Curves for Corrosion Rate Measurements of Steel in Stagnant NaCl Solutions
S. Wolynec and E. Escalante
Corrosion
in press

Corrosion Enhancement Due to Large Voltage Modulations. Frequency Analysis of the Response of Electrodes Under Charge-Transfer
U. Bertocci and J. L. Mullen
Proceedings of the ASTM Symposium on "Progress in Electrochemical Corrosion Testing"
in press

Underground Corrosion
E. Escalante
Corrosion and The Building Industry, National Association of Corrosion Engineers Publication
in press

A Qualitative Ellipsometric-Electrochemical Approach for the Study of Film Growth Under Organic Coatings
J. J. Ritter and J. Kruger
Surface Science
in press

Possibilities for Application of Fundamental Approaches to Technological Problems
J. Kruger
Surface Science
in press

The Morphology of Polycrystalline Steel Fibers Produced by Thermal Decomposition of Iron Pentacarbonyl in the Presence of a Magnetic Field
D. S. Lashmore, W. A. Jesser, and H. G. F. Wilsdorf
J. Appl. Phys.
in press

Adhesion of Electrodeposited Coatings
D. S. Lashmore
J. of Adhesion
in press

Studies of Passive Film Breakdown by Detection and Analysis of Electrochemical Noise
U. Bertocci and J. Kruger
Surface Science
in press

Applications of a Low-Noise Potentiostat in Electrochemical Measurements
U. Bertocci
J. Electrochemical Society
in press

Speciation of Trace De-and Triorganotins in Water by Ion Exchange HPLC-GFAA
K. L. Jewett and F. E. Brinckman
J. Chrom. Soc.
in press

Characterization of Bioactive Organotin Polymers Fractionation and Determination of MW by SEC-GFAA
E. J. Parks and F. E. Brinckman
Proceedings of the 7th International Symposium on Controlled Release of Bioactive Materials
in press

An Overview of the Anaerobic Corrosion of Underground Metallic Structures Evidence for a New Mechanism
W. P. Iverson
in press

Slag and Metal Oxide Vaporization in Reactive Atmospheres
J. W. Hastie, D. W. Bonnell, and E. R. Plante
High Temperature Science
in press

Radiations and Conduction Loss Corrections to Free Drop Calorimetry Data
D. W. Bonnell, A. J. Valerga, and J. L. Margrave
High Temperature Science
in press

Effect of Flame Boundary Layer in Line of Sight Optical Measurements
L. H. Grabner and J. W. Hastie
Combustion and Flame
in press

The Four-Ball Wear Test for Engine Oil Evaluation
R. S. Gates and S. M. Hsu
Proceedings-Joint Conference on Measurements and Standards for Recycled Oil/Systems Performance and Durability, NBS, S.P. #584
in press

Review of Laboratory Bench Tests in Assessing the Performance of Automotive Crankcase Oils
S. M. Hsu
Lubricating Engineering Journal
in press

Engine Oil Evaluation Through Bench Testing
S. M. Hsu
Proceedings of the Joint Conference on Measurements and Standards for the Recycled Oil/Systems Performance and Durability, NBS, S. P. #584
in press

Characterization of Lubricating Basestocks
S. M. Hsu
Proceedings of the Joint Conference on Measurements and Standards for the Recycled Oil/Systems Performance and Durability, NBS, S. P. #584
in press

Characterization of Re-refined Lubricating Base Oils
S. M. Hsu and D. A. Becker
A Society of Automotive Engineer
in press

Temperature Profiles of Inhibited Flames Using Raman Spectroscopy
M. C. Drake and J. W. Hastie
Combustion and Flame (in press)

Division Seminars

The Division Seminar Program has endeavored to arrange two talks each month; one by a speaker within the Bureau and a second by a speaker from outside. Responsibility for providing speakers rotates amoung the Group Leaders. It has not been possible to follow the idealized schedule exactly; however, we have had 31 talks scheduled in FY80, of whom all but three were speakers from outside. A chronological list of talks follows:

Ion Transfer Reactions at Metal Electrodes and the Structure of the Surface
K. E. Heusler
Technische Universität Clausthal-Zellerfeld, West Germany
September 18, 1979

NMR Studies of Alkylated Coal
L. Alemany
University of Chicago, Chicago, Illinois
October 23, 1979

Chemical Models for the Environmental Transmethylation of Metals
J. S. Thayer
University of Cincinnati, Cincinnati, Ohio
October 25, 1979

Recent Advances in the Chemistry of Simple and Bi-Metallic Alkoxides
R. C. Mehrotra
University of Delhi, Delhi, India
November 7, 1979

Ester Oxidation at High Temperatures
F. Lockwood
General Motors Company, Michigan
November 16, 1979

Effect of Alternating Current on Corrosion of Low Alloy and Carbon Steels
D. A. Jones
University of Nevada-Reno, Reno, Nevada
November 30, 1979

Toward the Preparation of an "Atlas of Chemical and Electrochemical Equilibria in the Presence of a Gaseous Phase"
M. Pourbaix
CEBELCOR, Brussels, Belgium
December 6, 1979

Ionic Transport Studies of Fluorites
A. Chadwick
University of Kent, Canterbury, England
January 8, 1980

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E. McCafferty
Naval Research Laboratory
January 24, 1980

The Melting Behavior of Small Particles of Tin, Indium, and Bismuth
W. A. Jesser
University of Virginia, Charlottesville, Virginia
January 25, 1980

Chemical Additives and Their Role in Automotive Lubrication
J. Udelhofen
Amoco Chemicals Research Center, Naperville, Illinois
January 30, 1980

Infrared Emission Spectra From an Operating Bearing--Generation, Dependence on Operating Conditions, and Interpretation
J. A. Lauer
Rensselaer Polytechnic Institute, Troy, New York
February 1, 1980

Erosion-Corrosion Processes
J. Zahavi
Institute of Metals, Technion, Haifa, Israel
February 25, 1980

Dynamic Control of Particle Size Distribution and Agglomeration in the Continuous Precipitation of Zirconium-Yttrium Hydroxides
L. E. Burkhart
Iowa State University, Ames, Iowa
March 4, 1980

Strain-Rate Effects in Environment-Sensitive Fracture
R. N. Parkins
The University of Newcastle-Upon Tyne, England
March 13, 1980

Penn State Micro-Oxidation Project Review
E. E. Klauss
Pennsylvania State University, State College, Pennsylvania
March 17, 1980

The Electrochemistry of Wrecks
I. D. MacLeod
Western Australian Museum, Australia
April 3, 1980

The Coordination and Solution Chemistry of Benzothiazole-2-Thiol, -Selenol, Dialkyl and Diaryl-dithiophosphates, and Dithiophosphinates
J. A. McCleverty
Department of Chemistry, Univeristy of Sheffield, Sheffield, England
April 7, 1980

Some Aspects of the Formation of Hydrides in Metals
B. Muddle
University of Illinois, Urbana, Illinois
April 16, 1980

The Mechanism of Stress-Corrosion Cracking and Corrosion Fatigue of Austenitic Stainless Steels in Dilute Environments
F. P. Ford
General Electric Company, New York
April 23, 1980

Use of Impedance Spectroscopy in Studying Solid Electrolytes
A. D. Franklin
Division 561, NBS
May 6, 1980

Electrochemical Noise
U. Bertocci
Division 561, NBS
May 16, 1980

Surface Analysis of Electrodes
J. Brace
University of Paris, France
May 19, 1980

The Electrochemistry of the Oxygen Electrodes
S. Srinivasan
Brookhaven National Laboratory, Long Island, New York
May 20, 1980

Applications of Pyrolytic Methylation/Gas Chromatography in Organic Analyses
W. C. Kossa, Jr.
Pennsylvania State University, State College, Pennsylvania
June 2, 1980

Use of Neutron Scattering to Study Hydrogen Effects in Metals
K. Hardman
NBS
June 23, 1980

High Temperature Chemistry of Phosphorous-Containing Flames
J. W. Hastie
Division 561, NBS
July 16, 1980

Diagrams of Chemical and Electrochemical Equilibria for the Systems,
O, H, Fe, O-H-Fe
M. Pourbaix
CEBELCOR, Brussels, Belgium
July 17, 1980

The Application of Metal Vapor Lasers to Raman Spectroscopy for
Gas and Flame Diagnostics
I. Glatt
The Atomic Energy Commission, Israel
July 21, 1980

Recent Progress in High Temperature Microwave Spectroscopy
T. Torring
Freie Universität, Berlin, Germany
July 31, 1980

Recent Developments in the Applications of ESCA to Corrosion Science
J. E. Castle
University of Surrey, Guildford, England
August 4, 1980

Localized Corrosion Behavior of Glassy Chromium Containing Alloys
R. B. Diegle
Battelle Memorial Laboratory, Columbus, Ohio
August 22, 1980

Metal Cluster Chemistry: Simulation of Corrosion Inhibition
Y. Jeannin
Universite Pierre et Marie Curie, Paris, France
August 25, 1980

Chemistry and Sterochemistry of Fluorophosphoranes: Recent Advances
R. Schmutzler
Technische Universität Braunschweig, West Germany
September 19, 1980

External Recognition

Case Centennial Scholar
Case Western Reserve University
June 2-3, 1980
E. N. Pugh

Captain Alfred E. Hunt Award
American Society for Lubrication Engineers
San Francisco, California
August 1980
S. M. Hsu

Case Centennial Scholar
Case Western Reserve University
October 20-22, 1980
J. Kruger

1980 Gordon Research Conference on Corrosion
Invited Speakers--J. J. Ritter and E. N. Pugh
Discussion Leader--J. Kruger

1980 Gordon Research Conference on Physical Metallurgy
Discussion Leader--A. D. Franklin

1980 Gordon Research Conference on High Temperature Chemistry
Discussion Leader--E. R. Plante

1980 Gordon Research Conference on Lubrication, Friction, and Wear
Invited Speaker--S. M. Hsu

IR 100 Award
Industrial Research and Development Magazine
Transpiration Mass Spectrometer
1980
D. W. Bonnell and J. W. Hastie

Books

Characterization of High Temperature Vapors and Gases
Edited by J. W. Hastie
Proceedings of the 10th Materials Research Symposium, NBS, September 18-22, 1979
NBS SP 561, 2 Vols., 1726 pages
1980

Early Pyrotechnology
Edited by T. Wertime, A. Franklin, and J. Olin
Proceedings of a Seminar, April 19-20, 1979
in press

Special Reports

Passive Films, Surface Structure, and Stress Corrosion and Crevice Corrosion Susceptibility
J. Kruger, J. J. Carroll, A. J. Melmed, J. J. Ritter, and J. R. Ambrose
NBSIR 79-1904 (Report to the Office of Naval Research), Technical Summary Report No. 9 (November 1979)

Materials for Fuel Cells
L. H. Bennett, C. K. Chiang, M. I. Cohen, A. L. Dragoo, A. D. Franklin, and A. J. McAlister
NBSIR 80-1991 (Report to Division of Fossil Fuel Utilization, DOE) (Annual Report January 1978-December 1978--issued March 1980)

Development of *In Situ* Techniques for the Detection and Measurement of Corrosion of Copper Concentric Neutrals in Underground Environments
J. Kruger, U. Bertocci, E. Escalante, and J. L. Mullen
NBSIR 80-2083 (Report Prepared for DOE, January 1980)
Final Issued June 1980

Measuring The Rate of Corrosion of Reinforcing Steel in Concrete
E. Escalante, S. Ito, and M. Cohen
NBSIR 80-2012 (Annual Report prepared for the Federal Highway Administration) (March 1980)

Anodizing and Immersion Processes
D. S. Lashmore
NBSIR (Report to Aluminum Association)
in press

Passive Films, Surface Structure and Stress Corrosion and Crevice Corrosion Susceptibility
J. Kruger, J. J. Carroll, A. J. Melmed, and J. J. Ritter
NBSIR (Report to the Office of Naval Research) Technical Summary Report No. 10
in press

A Review of Techniques for Measuring the Corrosion of Metals in Concrete
E. Escalante
NBSIR (Report to the Federal Highway Administration)
in press

Use of the Slow Strain Rate Technique for the Evaluation of Structural Materials for Application in High Temperature Gaseous Environments
G. M. Ugiansky and C. E. Johnson
NBSIR
in press

Molecular Chemistry of Inhibited Combustion Systems
J. W. Hastie and D. W. Bonnell
NBSIR (Final Report to Army)
in press

Materials for Fuel Cells
C. K. Chiang, M. I. Cohen, A. L. Dragoo, and A. D. Franklin
NBSIR (Report to the Division of Fossil Fuel Utilization, Department of Energy)
in press

Standard Reference Materials

The Division produces coating thickness SRMs, used to calibrate coating thickness gages. A single SRM is a metal coupon, 3 x 3 cm or 1.5 x 1.5 cm, one surface of which has an electroplated coating of certified thickness. Most of these are non-magnetic coatings on steel, but also included are nickel, gold, and tin coatings on various metallic substrates. Some 53 different SRMs are made ranging in thickness from 0.7 μm to 2 mm. (Gold coatings are actually certified in units of mass/area, not length.) They are designed for use with either magnetic type or beta backscatter type thickness gages.

These SRMs are packaged in sets and the SRM catalog lists some 31 different sets. About 3000 individual coating thickness standards were produced during FY79, and about 5000 were produced during FY80.

The Division is also in the process of developing NMR SRMs to be used for calibration of NMR spectrometers. A single SRM will consist of two seven-inch long NMR tubes, 5 mm and 10 mm (or 12 mm) in diameter, respectively. The tubes will contain a mixture of organic liquids sealed in an inert atmosphere and will be calibrated for proton line positions (five lines) and carbon-13 line positions (eight lines). It is expected that the initial stock will consist of 200 NMR tubes.

Patents

Frequency Stabilized Laser
R. B. Green, R. A. Keller, G. G. Luther, P. K. Schenck, and J. C. Travis
January 15, 1980
U. S. Patent 4,184,127

Sponsored Conferences

Regional Workshop on Corrosion Resources Panel for Managers
of Regional Economic Development--Coastal Zone--Georgia to New Jersey
Wallops Island, Virginia
June 20, 1980
J. Kruger

Gordon Research Conference: High Temperature Chemistry
Plymouth, New Hampshire
August 4-8, 1980
J. W. Hastie

Ceramics as Archeological Material
Smithsonian Institution and NBS, Washington, DC
September 29-October 1, 1980
A. D. Franklin and J. Olin

DIVISION

FRACTURE AND DEFORMATION DIVISION

Richard P. Reed, Acting Chief
Sheldon M. Wiederhorn, Deputy Chief
D. C. Shields, Administrative Assistant
C. J. Montgomery, Secretary
P. L. Salpino, Secretary
D. L. Mills, Secretary

Structures and components must be mechanically reliable. A significantly large portion of our Nation's effort to ensure public safety and environmental quality concentrates on material and structural mechanical integrity. Our Nation pays a high cost because materials fracture; careful design, structural codes and standards, material development and characterization, quality control and inspection, and the replacement, inconvenience, injuries, and deaths from unexpected failures all contribute to this cost. The principal goal of the Fracture and Deformation Division is to minimize material failure.

There are three essential research thrusts to reduce material failure (1) theory and modeling of deformation and fracture, (2) mechanical characterization, and (3) fracture-mechanics development and application. For comprehensive insight, the mechanisms of deformation and fracture must be understood. Characterization of material mechanical performance is essential for the proper development and selection of materials for service application and for efficient design that takes full advantage of the performance of the selected materials. Fracture-mechanics development and utilization will provide quantitative assessment and standards for the integrity of critical structures by relating material mechanical behavior to flaw characterization and service environment. The emphasis of the research of the Fracture and Deformation Division focuses on the critical areas of these three thrusts. This emphasis is subsequently referred to as Tasks, which are discussed in this report.

The Division is conducting a study to assess the costs of fracture to the Nation. This study was mandated by the Congressional Subcommittees on Natural Resources and Environment and on Science, Research, and Technology of the House of Representatives Committee on Science and Technology. Even with the use of the currently best available design, fabrication, and inspection procedures, it sometimes happens that structures, mechanical components, and containers experience unintended fracture during use. The economic effect of unintended fractures and the costs to prevent fractures are expected to be large in the domestic economy. The documentation of these costs is one purpose of this study. A second purpose is to determine the economic benefits to be derived from wider application of existing fracture-control technology. The third purpose is to establish the economic impact of the utilization of improved understanding of fracture processes and the control of fracture and to identify specific areas requiring research emphasis.

Division personnel are located in both Boulder and Gaithersburg. Although separate geographically, these two groups complement each other. The Boulder group has emphasized low-temperature properties, especially mechanical, of metals, alloys, and composites. The Gaithersburg group has emphasized high-temperature mechanical properties, especially of ceramics, and failure analyses. Together these groups represent most of NBS's expertise in mechanical properties and all its expertise in fracture mechanics, a research activity now expanding at NBS.

The Division's technical outputs reach many government agencies, including the National Aeronautics and Space Administration (NASA) and the Departments of Energy (DOE), Transportation(DOT), and Defense (DOD). Recent emphasis on fusion, magnetohydrodynamics (MHD), coal gasification, and geothermal energy by the Department of Energy has led to several efforts: low-temperature research for structural containment of the large magnetic fields produced by superconducting magnets; an assessment of future low-temperature material requirements for superconducting MHD magnets; characterization of castable refractories at high temperatures and pressures; development of an in situ evaluation test for metal susceptibility to high-temperature, high-pressure environment-assisted metal cracking; property characterization of geothermal cements; and study of high-temperature deformation and crack growth of coal-conversion-system structural ceramics. Transportation-related research includes establishing inspection and alternative allowable-defect-size standards for pipeline girth welds, mechanical-property and microstructural characterization of pressure-tank-car steels and railroad wheels, fracture-mechanics assessment of tank-car behavior, development of test standards for lightweight compressed gas cylinders, and numerous structural metal-fracture analyses. Research for the Department of Defense is diverse. We assist the Navy in upgrading its fracture-control plans, identifying material limitations in ultrasensitive inertial-guidance-system gyroscopes, studying the applicability of proof testing to nitride and carbide ceramics that may be used in gas-turbine engines, conducting erosion and wear experiments of ceramics to reduce machining costs, and examination of the low-temperature material properties related to superconducting motors and generators for ship propulsion. We assist the Air Force in using advanced composites in lightweight-superconducting-magnet, airborne power packages. The creep, fracture toughness, strength, and elastic properties of several alkali halides are being studied to assist NASA in proper selection of the scintillation material for the NASA Gamma Ray Laboratory.

The Division hosts and leads a number of workshops and conferences each year. Collaborating with the DOE, annual workshops on "Materials at Low Temperatures" are hosted each year at Vail, Colorado. The Mechanical Failure Prevention Group hosted two conferences: "Failure Prevention in Ground Transportation Systems" and "Failure Prevention in Pipelines." With the American Welding Society our Division cosponsored the conference on "Fitness-for-Service of Welded Structures." The Division actively leads and supports the International Cryogenic Materials Conference, which held its annual meeting in Geneva, Switzerland, on "Nonmetallic Materials at Low Temperatures."

New opportunities for research have been provided in the Division by the NBS Durability Program. Increased emphasis has been placed on elastic-plastic fracture mechanics. Workmanship codes need to be extended to fitness-for-service alternatives to reduce repair welds, to assess specific defects in critical structures, to formulate fracture-control plans for critical structures, and to estimate structural-integrity lifetimes. Elastic-plastic fracture-mechanics models and methodologies are needed to replace the traditional linear-elastic fracture-mechanics approach because most structural alloys for critical applications are selected to ensure against crack instability preceding plastic deformation. Therefore, research has been initiated on test methodologies, model development and verification, and effects of defects and subcritical crack growth; all of these relate to elastic-plastic or all-plastic conditions.

New studies have also been started on high-temperature or time-dependent properties of metals. Such research is timely because new energy-conversion systems, plasma-containment systems, and nuclear systems all have serious material-selection and durability problems associated with understanding and characterizing the time-dependent fracture processes in structural alloys. Study of crack-tip fracture mechanisms, characterization of fracture processes, and generation of property data (emphasizing creep and fatigue), will provide new insights to assist in high-temperature design and material selection.

Three principal research tasks have been established to emphasize the research directions Division:

12121	FRACTURE MECHANISMS AND ANALYSES
12122	DURABILITY OF CERAMICS AND COMPOSITES
12123	ELASTIC-PLASTIC FRACTURE MECHANICS

Research within our Division is discussed under Subtasks of these. Tasks 1 and 3 have received greater emphasis from the opportunities under the Materials Durability Program, and Task 2 emphasizes research directed toward mechanical performance of the very promising major material classes: ceramics and composites.

FRACTURE MECHANISMS AND ANALYSES
Task 12121

For structural materials, the basics of crack-tip processes are essential to understanding fracture and predicting its long-term effects. Influences of atomic structure and chemical reactions at the crack-tip have been demonstrated with atomistic models of fracture in a solid, but these influences have not yet been confirmed quantitatively by experimental studies of subcritical crack growth and environmental effects. Ductile processes in the high-stress region of the crack tip must be introduced into these atomistic models to assess the role of plastic deformation and to extend the theoretical models to describe crack-growth phenomena such as fatigue. High-temperature fracture is complex: competitive fracture mechanisms, such as subcritical crack growth, cavity nucleation and growth, and grain-boundary sliding, are affected by microstructure, impurity content and segregation, processing history, and environment.

Failure-analysis studies perform a valuable service for those Government agencies that have no testing facilities and require research on the safety of structural materials. By using modern metallographic, x-ray, fractographic, and chemical-analyses techniques, and maintaining a Failure Information Center, our Division serves as a focal point for analyses and compilation of many critical structural failures.

The NBS Materials Durability Program has provided funding for increased emphasis on high-temperature fracture processes and mechanisms Our understanding of the fracture of metals under time-dependent conditions will be increased by research on crack-tip theory coupled with high-temperature tensile, creep, and fatigue properties.

Research in Fracture Mechanisms and Analyses is divided into five areas: Fracture Theory, Time-Dependent Fracture Processes, Failure Information Center, Failure-Avoidance Services, and Plastic Deformation of Metals.

Fracture Theory
Subtask 1 of Task 12121

T.-J. Chuang, R. deWit, R. J. Fields, E. R. Fuller, Jr., R. M. Thomson, S. M. Wiederhorn

Predictions of crack growth and fracture and, hence, of component reliability can only be attained rationally through a fundamental understanding of crack-tip structures and crack-tip processes. This desire for understanding at a fundamental level has provided considerable impetus to atomistic modeling of cracks and crack-tip processes. By reconsidering a one-dimensional lattice model of a crack, we were able to decouple effectively the nonlinear interatomic interactions in the crack-tip region from the linear elastic interactions in the bulk solid. This stratagem provides a mechanics model within which the influence of the crack-tip bond interaction can be explored, whether that interaction is intrinsic or chemically affected. Utilizing a Green's-function approach and the method of lattice statics, this analysis has been extended to more realistic crack configurations in two- and three-dimensional cubic lattices. The concept of partitioning the fracture phenomenon into two parts, one specific to the crack-tip region and another specific to the bulk elastic solid, remains as a general feature in these more realistic configurations.

Although these atomistic models demonstrate the existence of stress-dependent energy barriers to crack advance, and illustrate the influence of chemical interactions on these barriers, they do not address the kinetics of crack growth. To address this issue, kinetic theories of chemically assisted fracture were developed at two levels of sophistication. Both theories are couched in terms of classical "absolute reaction rate theory," but one represents a statistical-mechanical approach to fracture whereas the other represents an extension of chemical-reaction-rate theory. For the statistical-mechanical approach, expressions were derived for the crack-growth rate in a reactive gaseous environment. Specific results depend on the chemical system studied including both solid and gaseous species. But in general, atmospherically assisted fracture is associated with a reduction in the surface energy due to adsorption. The chemical approach agrees conceptually with the statistical mechanical approach, but treats the solid as an elastic continuum and the bond rupture process at the crack tip as a chemical reaction. A basic equation from chemical reaction rate theory was extended to account for both the high tensile stress fields and the highly curved surfaces in the crack-tip region. When compared with experimental data for silicate glasses, this expression gives a crack growth rate that is proportional to the chemical activity of the reacting species, predicts a stress dependence in agreement with activation volumes, and gives an activation energy in agreement with silica-network dissolution data.

At lower temperatures, failure results primarily from chemically assisted subcritical crack growth. As the temperature increases, however, creep deformation and creep crack growth become important elements of the high-temperature failure process. With the initiation of experimental studies in this area, we have begun to consider models of crack growth in a creeping material. When the creep behavior is localized to the crack-tip region, a strain-rate dependent zone correction (analogous to the plastic zone correction used by Irwin for small scale yielding) adequately describes the strain-rate dependence of the high-temperature toughness. When the creep behavior is not localized, however, a more detailed account must be taken of the influence of time-dependent deformation on the fracture process. In this regard we have reviewed two recent manuscripts on this subject (one by C. Y. Hui and H. Riedel, and another by E. W. Hart), and are pursuing the nature of apparent discrepancies in their results.

Often our ability to assess a material's behavior in different environments and temperature regions depends as much on the form in which we present the engineering information as on the information itself. During the past year, a different method of expressing crack-growth data has been developed that clearly delineates mechanisms of crack growth as a function of temperature and stress-intensity factor. Contours of constant material response, namely, crack-growth rate, are plotted on a diagram of the experimentally controllable parameters: temperature and stress-intensity factor. This type of representation emphasizes changes in a material's fracture mechanism as either the temperature or the stress-intensity factor change, and thereby displays the variety of ways that cracks can grow in a material. We have used these crack-growth-mechanism maps as an aid in the critical evaluation of elevated-temperature crack growth and fracture data. They provide a broad and self-consistent picture of a material's resistance to crack growth and clearly indicate regions where data either is missing or is contradictory. These maps have been prepared for a number of materials including a nickel-base superalloy, an aluminum alloy, a hot-pressed silicon nitride, and a number of silicate glasses.

Time-Dependent Fracture Processes
Subtask 2 of Task 12121

B. W. Christ, J. G. Early, R. deWit, R. J. Fields, S. W. Freiman, E. R. Fuller, Jr., G. E. Hicho, C. G. Interrante, R. S. Polvani, S. R. Low

Crack growth experiments are being conducted in controlled atmospheres to provide experimental corroboration with our atomistic theories of chemically assisted crack growth. An optimum selection of material, environment, and temperature is necessary to ensure chemical absorption at the crack tip and yet to prevent complications that result from crack-tip dislocation processes. Accordingly, initial experiments have been directed towards characterizing the crack growth behavior of a soda-lime-silicate glass as a function of temperature in vacuum and in gaseous environments of argon and argon with two percent hydrogen. Since chemically assisted crack growth in this material is generally attributed to the presence of water vapor, these experiments will help to clarify the role, if any, of hydrogen. Further studies will be conducted on two materials: fused silica, a material that exhibits moisture-assisted crack growth, but does not exhibit crack growth in vacuum; and single crystal silicon, a material that does not appear to exhibit any type of subcritical crack growth.

Another area of time-dependent response that we have begun to examine this year is creep-assisted crack growth at high temperature. As part of this effort we have been characterizing the creep-cavitation behavior ahead of a growing crack in copper and in a high-temperature structural alloy. Either a center-cracked panel or a single-edge-notched tensile specimen is subjected to an applied load at elevated temperature to extend the crack by creep-crack growth. The distribution of cavities around the crack tip is then characterized using automated quantitative metallographic techniques. These studies will help to provide an understanding both of the creep cavitation behavior in the highly nonuniform stress field ahead of a crack and of how these cavities contribute to the crack-growth process.

In another area of research, a comparison is being made among various methods for determining the amount of high-temperature crack growth. For this purpose, compact tension specimens of an aluminum alloy have been prepared and heat treated to fracture in a creep-brittle manner. Five methods are being considered for measuring the extent of crack growth: (1) a compliance technique; (2) an electrical resistance technique; (3) a crack-mouth-opening-displacement measurement; (4) a visual measurement on the side of the specimen; and (5) an actual crack-length measurement by sectioning through the thickness. Ultimately, these techniques will be applied to high-temperature crack growth in a high-chromium ferritic stainless steel.

An objective of this subtask is to investigate and improve test methods in two generic categories: (1) those that are used in studies of fracture processes that are governed by an environmental effect on a material under sustained loading conditions and (2) those that may be influenced by a strain-rate sensitivity of the material of test. As a counterpart to this objective, these methods are applied to significant materials problems.

In the area of sustained load testing, the problem of hydrogen embrittlement of steels has been a focus of studies. As a result of past efforts, studies have been published on (1) a method for measurement of the permeation of hydrogen in metals, (2) a method for removal of sulfides from fracture surfaces that have been exposed to aqueous sulfide environments, and (3) studies of the effect of temper embrittlement of steel on the susceptibility of steel to hydrogen embrittlement.

This year, attention has been centered on completing work on development of an automated real-time method of analysis of crack-growth rates of steels tested in aggressive aqueous environments. This method has been applied to study the behavior of 2.25 CR - 1.0 Mo steels tested in an acetic solution containing H_2S at one atmosphere of pressure, using the double cantilever beam (DCB) type of fracture-mechanics test specimen using the test methods and data acquisition system that were developed in these studies. Crack-growth-rate data were obtained for various conditions of test to determine the effects of specimen orientation, methods of specimen preparation, and steel hardness. Work is underway on the development of a suitable test method to assess environmental conditions that promote the formation of branch cracks in DCB specimens tested in a severe sulfide environment. These studies have been conducted under the guidance of the Subcommittee on Hydrogen Embrittlement of the Pressure Vessel Research Committee of the Welding Research Council (WRC). Work on an interpretive report to be published in about a year from now as a WRC Bulletin on The Effects of Hydrogen on Pressure Vessel Steels was initiated this summer.

Impact-test studies have been centered on the measurement of fracture toughness using both pendulum and drop-weight tests. Pendulum testing includes tests of both standard and precracked Charpy-V-notch (CVN) specimens. Drop-weight testing includes dynamic-tear (DT) tests and drop-weight NDT tests. Test-method development activities have involved methods for computer-assisted testing and data analysis for these impact tests. The studies include analyses of several alternative methods for the measurement of energy absorption in DT and CVN tests. Applications in which impact testing has been used to serve Government agencies include works on plate materials used for railroad tank cars, structural steels used in highway bridges, and plate materials used in pipelines. The results of impact tests are often useful for fracture control, based upon either service experience or empirical correlations with fracture-mechanics tests.

<u>Failure Information Center</u>
Subtask 3 of Task 12121

R. C. Dobbyn, W. A. Willard

The Failure Information Center assists the coal-conversion industry in extending the useful life and reliability of plant components by maintaining a central source of information on the performance, especially failures, of materials and components used in coal conversion environments. It provides an integrated material-properties data base for construction materials to aid in the design, construction, and operation of coal-conversion plants. Finally, it collects and evaluates the information, maintains computer files for convenient retrieval, and disseminates the data in convenient form to users.

Sources of the information compiled by the Failure Information Center include operators of all gasification and liquefaction processes, from bench-scale units through operating pilot plants participating in the DOE voluntary failure reporting program. Information detail varies from one-page failure-occurrence reports to final reports of laboratory analyses of failed parts.

A computerized data base of approximately 500 reported failures has been established and is continually being updated, refined, and increased as additional failure reports are received. Separate information items addressing the same failure are collated when possible. In addition, direct contact with operating personnel at the various process locations and with failure analysis laboratory staff has enhanced the quality and the flow of information and has assisted plant operators in problem solving.

At present, the Center produces sets of abstracts covering all reported incidents. The abstracts are intensive summaries constructed from the source document and they contain all reported data. They are sorted according to material, component type, failure mode, and conversion process, or any combination of these factors.

Although fewer pilot plants are now operating, resulting in a very slow rate of increase of the data file, there is continuing interest on the part of the user community. Some 1100 reports and about 30 data tables and abstracts summarizing in-service materials and components performance were sent out in response to over two dozen requests. An interpretive report, analyzing erosive wear failures, has been published as an NBS internal report and has also been submitted to DOE for publication in their report series. Information is regularly supplied for the Failure Experiences feature of the DOE Materials and Components Newsletter, published by Battelle-Columbus.

The major effort for the past year has been a joint project with the Materials Properties Data Center in the preparation of a publication, Construction Materials for Coal Gasification--Performance and Properties Data, currently submitted to DOE for approval. This book contains information gained in practical plant experience and also the results of materials research and testing programs. It deals with the information in the context of eleven separate component areas of coal gasification plants, and draws from this information an indication of possible candidate materials of construction. A separate section of the book includes extended data for the chemical, physical, and mechanical properties of the candidate materials. The book will consist of loose-leaf pages so that increasing and revising the data can be done readily on a regular basis.

Failure-Avoidance Services
Subtask 4 of Task 12121

J. H. Smith, J. G. Early, T. R. Shives, G. E. Hicho, W. A. Willard, B. W. Christ, C. G. Interrante

Failure-avoidance services provided to other Government agencies and other Divisions within NBS include diagnostic failure analysis, mechanical-properties testing, metallographic analysis, and metallurgical consultation. The results of this work have been used to assist in the development of safety regulations, in the selection of improved materials to improve the reliability of components and structures, and the development of improved test methods and standards. In many cases, diagnostic failure analysis of failed components has led to the identification of needed research in materials characterization and this research is now part of the ongoing programs described in this report. During the present year, some 30 reports of specific projects in failure analysis and failure avoidance have been completed. As in previous years, projects have been completed for the National Transportation Safety Board, the Consumer Product Safety Commission, the Bureau of Engraving and Printing, the Federal Railroad Administration, and the Office of Hazardous Materials. Also, special projects were completed for eight other Federal agencies. Reports of these investigations are shown in the list of publications in this report.

Diagnostic failure investigations for the National Transportation Safety Board (NTSB) were completed on several aircraft components and on several sections of failed gas pipeline. The results of these investigations are used by NTSB to identify potential hazards in transportation systems and to advise the Department of Transportation on the need for improved safety regulations.

Investigations for the Consumer Product Safety Commission (CPSC) included analysis of bicycles, lawn mowers, hardware items, and copper tubing. The results of these investigations are used by CPSC to assess the need for modifications to the design or materials used in these products to reduce the risk of injury to the public.

Continuing work for the Bureau of Engraving and Printing (BEP) has successfully identified the cause of failure in printing plates and other components in the presses used to print money and postage stamps. The results of these investigations have resulted in improved specifications for purchasing the materials and fabricating these components so that failures in the BEP printing presses have been essentially eliminated.

Recent investigations on several metallic components used for implantation during surgery have been completed for the Food and Drug Administration. Identification of the cause of premature failure in these components is essential to improving the reliability of these components.

A major investigation to identify the cause of cracking in welds in the replacement Silver Bridge at Point Pleasant, West Virginia, has been completed for the Federal Highway Administration. The results of this investigation will be used by the Federal Highway Administration to specify materials requirements, welding procedures, and weld-repair procedures to be used in future bridge construction. Weld cracking has been identified as a problem in several large bridges recently constructed throughout the interstate highway system. Identification of the causes of these cracks and the specification of corrective measures is an urgent national problem.

Continuing work for the Federal Railroad Administration has identified the causes of failure in railway tank cars and in suggesting improved materials to resist fracture in the event of tank-car accidents. The extreme hazard resulting from frequent accidents involving tank cars containing hazardous materials is a national problem of growing significance. Results of the NBS work on tank-car materials have assisted in the development of specifications for new tank cars which significantly reduce the frequency of major tank-car accidents.

Besides these major failure-analysis investigations, a wide range of other projects was completed. Determination of the cause of failure in several types of fasteners was completed for the Coast Guard, the Navy, and the National Oceanic and Atmospheric Administration. Failure investigations were completed on failed piping and pressure vessels for the Materials Transportation Bureau (MTB) of the Department of Transportation. The results of these investigations are used by MTB to develop a data base on failure experiences in pressure vessels and piping and to determine if modifications to their safety regulations are required. For the Department of Justice, an investigation of the mechanical properties and strength of fencing used along the U.S. and Mexican border was completed. The results of this investigation may be used to develop more suitable specifications for the procurement of this fencing.

The dissemination of information to assist in Failure Avoidance was continued by NBS sponsorship of two meetings of the Mechanical Failures Prevention Group (MFPG) and the publication of the proceedings of these meetings. A meeting with the theme "Advanced Composites--Design and Application" was held in October 1979 and emphasized the use of new composites and identified means to prevent failure and improve the durability of components made from composites by proper design, materials selection, and inspection. The April 1980 meeting of the MFPG was on "Ground Transportation Systems" and provided a forum for discussion of methods of failure avoidance in bridges, pipelines, automobiles, and railway equipment.

<u>Plastic Deformation of Metals</u>
<u>Subtask 5 of Task 12121</u>

B. W. Christ, R. S. Polvani

Tensile microcreep in various metals and alloys is being measured currently on instrument-grade beryllium. The overall goals of this study are: (1) to develop a data base on microcreep (10^{-12} cm/cm·s) for improved design of gyroscopes used in inertial-guidance systems for naval applications, and (2) to develop a fundamental understanding of microcreep. This program involves combined efforts of two NBS groups and the C. S. Draper Laboratory, Cambridge, Massachusetts.

Microcreep testing of instrument-grade beryllium has been carried out at about 63 °C (145 °F). Temperature control is held to ± 0.005 °C (0.01 °F) on two testing systems designed to detect strains in the range of 10^{-7}. A third testing system designed to detect strains in the range, 10^{-8}, operates at a temperature of 40 °C (104 °F) with temperature control of ± 0.001 °C (0.0018 °F). Testing methodology is being developed to promote alignment control for microcreep tests in the stress range, 0.689 to 6.89 MN/m^2 (100 to 1000 psi) microstrain hardening, as well as microcreep rates, is of interest. A testing system for measuring microcreep rates under biaxial loading has been designed and built.

Initial results show that I-400 grade beryllium exhibits a microstrain of about 4 x 10^{-6} in 1000 hours at a stress of 20.67 MN/m^2 (3000 psi). The predominant deformation mechanism seems to be dislocation glide.

DURABILITY OF CERAMICS AND COMPOSITES
Task 12122

The Fracture and Deformation Division program on ceramics and composites has as its objectives five separate goals: (1) generation of new theory and data to elucidate fracture and deformation mechanisms in nonmetallic materials; (2) development of new techniques for studying the fracture and deformation properties of materials; (3) collection of engineering data for structural applications; (4) investigation of degradation processes that result in erosive and abrasive wear of nonmetallic materials; and (5) investigation of the microstructure of nonmetallic materials and their relationship to mechanical behavior. Experimental techniques developed by the Division permit measurements on the mechanical properties of composites and ceramics over a wide range of conditions: in vacuum at temperatures to 2700 °C in corrosive environments at temperatures that range from room temperature to 1600 °C, and in cryogenic environments at temperatures as low as -269 °C. This range of experimental capabilities is unique.

Ceramic materials are used where special properties, such as chemical resistance to corrosive environments, mechanical resistance to erosion and wear, and mechanical and chemical resistance to temperature extremes, are required. Ceramics, such as glasses, refractory concretes, geothermal cements, porcelains, and high-density ceramics, are used in many commercial applications, for example: containers for nuclear-waste disposal, linings for geothermal wells, components for high-temperature gas turbines and heat exchangers, thread guides and wear surfaces for the manufacture of paper and clothing, cutting tools and cutoff wheels for the shaping and finishing operations used in the manufacture of various machines and tools, and insulating linings for the coal-conversion and petrochemical industries. In defense applications, these materials are used as radomes, missile nose cones, turbine components in portable electric-generating facilities, and bearing surfaces in gyroscopes. Because they are brittle, structural ceramics are usually overdesigned to satisfy engineering requirements, or are not used, even though they have other outstanding properties. The investigation of the fracture and deformation properties of these materials may overcome many of the difficulties associated with their brittle behavior and permit ceramics to be used more effectively.

In contrast to metals or ceramics, composite materials are highly engineered, heterogeneous materials designed to impart unique, superior properties not achievable with conventional materials. Composites offer the possibility of high-strength, lightweight, durable structures. In typical advanced composites, the strength-to-weight ratio is an order of magnitude larger than normal grades of steel. Extensive commercialization of composites will realize major energy and materials savings, increased productivity, improved product safety, and improved U.S. technological innovative capabilities. The solution to effective industrial utilization of composite materials is a better understanding of their wear-out and fracture mechanisms. By investigating the mechanical strength and fracture behavior of a variety of composite materials (ceramic/ceramic, ceramic/metal, ceramic/polymer, and metal/polymer), many of the problems associated with mechanical degradation will be solved, and composites will be used in a wide variety of industrial applications for their unique properties.

Fundamentals of Fracture
Subtask 1 of Task 12122

S. W. Freiman, T. A. Michalske, E. R. Fuller, Jr., S. M. Wiederhorn

Studies are conducted to elucidate basic mechanisms of fracture and deformation in ceramic and composite materials. Because water plays such a dominant role in the stress corrosion of ceramic materials, most of the work during the past year was directed at understanding the role of water in the fracture process. The program is multifaceted, applying a variety of experimental techniques to this problem. Fracture-mechanics techniques and strength studies are used to understand the role of glass composition on the fracture process, whereas electron spectroscopy (chemical analysis) and Raman spectroscopy are used to identify the corrosion species and to investigate the effect of stress on the structure of ceramics. The program is approximately a three-man-year/year effort and involves collaboration between the Fracture and Deformation Division, and the Ceramics, Glass, and Solid State Science Division, and between our Division and Howard University. Details of this program are given below.

Surface Analysis: A new analytical technique, electron spectroscopy for chemical analysis (ESCA), is being applied to analyze chemical species that are formed on fresh surfaces of ceramic materials. Preliminary experiments were conducted during the past year on titanium to gain experience in using the ESCA apparatus and the NBS-designed deposition system for laying down thin coats of ceramic or metallic materials. Experiments consisted of the deposition and subsequent oxidation of metallic titanium. The oxidation process was analyzed using both 90° and angle-resolved ESCA. Studies showed that although oxidation occurred throughout the titanium, it occurred preferentially near the surface, as expected. The difference between surface and bulk oxygen in thin films was readily identified by peak shifts in the spectra using angle-resolved ESCA. Unfortunately, the effect of stress on the oxidation process could not be readily determined using the equipment as currently designed; consequently, the surface-analysis system is being modified to allow angle-resolved ESCA spectra to be obtained on stressed specimens.

Once these preliminary experiments are complete, and the equipment is operating satisfactorily, studies of water adsorption on ceramic substrates will be conducted. The effect of stress on the adsorption process will be studied by comparing the ESCA spectra obtained from thin films that are subjected to tensile stress with spectra obtained from stress-free films. To obtain such data, a tensile stage has been constructed that is capable of applying a stress to a thin film while it is being examined by the surface-analysis equipment. An apparatus was also constructed, with the help of the Surface Science Division, to admit precise amounts of water into the vacuum chamber for adsorption studies.

Within the coming year, we hope to use this apparatus for chemical analysis of stressed ceramics and glasses. This project is being conducted jointly with the Ceramics, Glass, and Solid State Science Division (D. M. Sanders).

Raman Spectroscopy: Raman-spectroscopy studies were conducted on fused silica fibers in order to determine the effect of stress on the structure of silica glass. It was observed that there were significant changes in peaks associated with defects in the SiO_2 structure under stresses of 2.1 to 3.4 GPa (300 to 500 ksi). These peaks were reproducible and have been ascribed to stretching of Si-O bonds. A talk on this work was presented at the annual meeting of the American Ceramic Society, and has now been written (S. W. Freiman, G. Walrafen, and P. N. Krishnan) and submitted for publication.

Crack-Growth Studies in Corrosive Environments: To investigate the relationship between corrosion of materials and subcritical crack growth, experiments were studied on several glasses in aqueous environments. The glasses varied greatly in their resistance to corrosion: chemical borosilicate glass and soda-lime-silica glass being the most durable; binary soda-silica compositions being the least durable. The effect of ion exchange on the crack growth process was investigated by conducting crack-growth studies in aqueous solutions containing either lithium or cesium ions. No significant effect of these ions on crack growth in the durable glasses was observed. By contrast, these ions had significant effects on crack propagation in the soda-silica glasses. The slope of the voltage-stress intensity (V-K_I) data was considerably greater when tests were conducted in solutions containing lithium ions. Perhaps the most significant observation was the existence of a low velocity (10^{-8} to 10^{-10} m/s) plateau for the soda-silica glasses. This plateau has been attributed to crack-tip blunting, and its existence confirms the theory of stress-corrosion cracking developed by Charles and Hillig.

Crack Growth in Phase-Separated Glasses: Crack growth experiments were also carried out in phase separated sodium borosilicate glasses that had been heat treated to vary the size and chemical composition of the phase-separated regions. It was observed that the V-K_I curves shifted to lower stress intensities as the heat-treatment time and the microstructure size increased. This behavior was interpreted in terms of the decrease of the chemical durability of the silica-rich phase due to an increase in Na_2O content of this phase. It was concluded that the microstructure size had little or no effect on crack growth since the crack always intersects both phases in the interconnected microstructure.

Proof Testing: To evaluate the effect of multiregion crack growth on component reliability after proof testing, soda-lime-silica glass was used as a model material in a set of proof-test studies that was conducted in normal pentane. Normal pentane was used to magnify the effect of multiregion crack growth because of the rather broad region-II crack-growth behavior in this liquid. Results were compared with a detailed theory of proof testing developed during the previous year's work; modest agreement between theory and experiment was obtained. The results from this study indicate that proof testing should be conducted in a dry gaseous environment using a rapid rate of unloading from the proof test load. If this procedure is not followed, a substantial number of components are liable to fail at loads that are less than the proof-test load.

New Approaches to Fracture and Deformation Information
Subtask 2 of Task 12122

E. R. Fuller, Jr., S. W. Freiman, S. M. Wiederhorn, R. J. Fields, N. J. Tighe

The techniques of fracture mechanics provide engineers with new methods for estimating the total allowable lifetime under load when mechanisms of failure are well understood. For ceramic materials, the primary mechanism of failure at low temperatures is subcritical crack growth, whereas that occurring at high temperatures is creep and creep cracking. By characterizing creep and fracture processes in ceramic materials, estimates of the creep rate or the crack-growth rate can be made, and the lifetime of structural components can be determined. The success of this approach depends, in part, on the quality of the creep and crack-growth data used to characterize the fatigue behavior.

For creep experiments pneumatic loading is being substituted for dead-weight loading. The pneumatic system has several advantages over the dead-weight system. It is inexpensive and compact; a number of systems can be used simultaneously for experimental purposes without requiring a great deal of space for operations. In addition, since compressed air is used to transmit load to components, the test system has a low inertial mass and is therefore insensitive to shocks or vibrations that may be present in the laboratory. Consequently several test fixtures can be mounted in a single furnace to conduct strength experiments without fear of interference between the separate fixtures. These advantages were used in the construction of a high temperature fracture-mechanics facility, which was designed so that three loading fixtures can be operated in each furnace. A similar facility is now nearing completion for evaluating the creep resistance of refractory materials for regenerative heat exchangers in large MHD facilities.

A pneumatic-loading facility has also been constructed as an integral part of our bioceramic test program. Here the compactness of the system has an advantage for the construction of a multiple-test facility that has the proper biological environment for testing materials intended for use as prosthetic devices. The equipment for the bioceramic program will be monitored through the use of a computer. The computer will automatically monitor the load, time under load, and temperature of the experiment, and will store these parameters until requested by the operator.

Two techniques for analyzing strength data in terms of fracture-mechanics parameters have been developed. An analysis was developed to determine crack-growth rates from static-fatigue (i.e., sustained-load) data. It is straightforward to calculate the time-to-failure at a given applied-stress level if the nucleation and crack-growth behavior are known. The inverse analysis is not straightforward. This inverse analysis was developed under the assumption that nucleation times are negligible and that failure times at stress are determined solely from crack-growth behavior. The analysis gives excellent agreement with measured data for a soda-lime silica glass.

In the second technique, the four-point bend test was analyzed to obtain crack-velocity data as a function of linear stress-intensity factor from a load-displacement curve. In a linear elastic material the load should be linear with displacement. If this is not the case (e.g., ceramics at elevated temperatures) then either the crack has grown, changing the specimen compliance, or the specimen has deformed plastically. Considering these possibilities for high-temperature structural ceramics, sensitive measurements were performed on hot-pressed silicon nitride at 1200 °C. Less than one percent permanent strain was detected in this material in the region of the final fracture. Therefore it was concluded that the nonlinear load-displacement curves were due to crack growth and the concomitant change in compliance. Consequently the compliance was calculated as a function of crack length for the four-point bend test. Using the calculated expression, the crack velocity and stress-intensity factor can be determined at any point on the load-displacement curve even when the stress-intensity factor is changing rapidly. It is possible to use this analysis to measure transient phenomena as well as steady-state phenomena that occur during crack growth. This technique of analysis provides a new means of collecting data on materials that exhibit crack-growth behavior at elevated temperatures.

Engineering Evaluation of Ceramics
Subtask 3 of Task 12122

E. R. Fuller, Jr., N. J. Tighe, S. M. Wiederhorn, S. W. Freiman, R. S. Polvani, D. E. Roberts, C. L. McDaniel, R. F. Krause, Jr., G. E. Hicho

Extensive studies are being conducted on the strength of ceramic materials that are intended for use in a number of important commercial and defense applications. Materials being studied include: geothermal cements that will be used to line the wells that tap hot reservoirs of water deep within the earth, specialty ceramics that are intended for use in heat engines, dense ceramic materials for prosthetic devices, alkali halides for scintillation counters in deep-space NASA gamma-ray observatories, dielectric materials for ceramic capacitors intended for defense applications, and refractories for regenerative heat exchangers used in MHD applications.

Geothermal Cements: The program on geothermal cements was initiated to develop a laboratory test facility for screening candidate cementing materials that are to be used in finishing operations of geothermal well holes. The program provides the technical data necessary for an evaluation of the structural integrity of these cements after they have been exposed to high-pressure, high-temperature brine. The suitability of these cements for more costly tests in down-hole facilities will be evaluated for DOE. The program is divided into several tasks aimed at establishing the mechanical and physical properties of cements after they have been exposed to simulated geothermal environments. Properties include flexural and compressive strengths, strengths of cement pipe interfaces, and cement permeability at high pressures and temperatures. The equipment has been designed and built. Proposed procedures have been drafted and submitted to an American Petroleum Institute Task Group for evaluation. In response to the DOE program for the development of improved cements, other laboratories have submitted 22 cement formulations for examination. Measurements have been made of the compressive strength and tensile strength of the cements, of the shear-bond strength of the cement to steel, and of the permeability of cement to water. In a cooperative venture established with Los Alamos Scientific Laboratory, portions of all the cements involved in the exposure studies were forwarded to Dr. G. Cocks of the DOE Los Alamos Laboratories for microscopic examination.

High-Temperature Structural Ceramics: Because ceramic materials offer the potential for significant increases in operating temperature and efficiency for gas turbine engines, silicon nitride and silicon carbide are being considered by DOD and DOE for application in heat engines. The division is contributing to these programs by evaluating the applicability of proof testing as a method of ensuring the structural reliability of heat-engine components, and by studying the mechanisms by which these materials fail at elevated temperatures.

The objectives of the program on proof-testing are three-fold: (1) investigate long-term effects of high temperature on the strength of silicon carbide and silicon nitride; (2) determine the physical and chemical conditions that limit the applicability of proof-testing as a method of improving the reliability of these ceramics; and (3) characterize the conditions of environment and temperature that result in strength-impairing flaw generation in silicon nitride and silicon carbide. It is expected that this program will provide a base of experimental data upon which a modified theory of component reliability can be built.

To date, approximately 1500 specimens of various commercial grades of silicon carbide and silicon nitride have been tested. Strength tests were run at 1200 °C for exposure times as long as 1000 hours, on sets of specimens that were either load free, or subjected to an applied load during exposure. The study demonstrates a wide variability in the behavior of these materials, the variability depending on the type of material, the process used for manufacture, and the particular lot or billet from which the material was derived. Despite the variability in the data, certain trends were observed that suggest a course of action for modification of theories of component reliability.

At one extreme of behavior, reaction-bonded silicon nitride became stronger with exposure to air at 1200 °C. Specimens that were subjected to an applied load either failed immediately, or survived the entire 1000-hour exposure without failing, suggesting that delayed failure does not occur in this material. The strength of the survivors greatly exceeded the strength of specimens tested without high-temperature exposure. This result suggests that higher temperatures modify the flaw structure of the material to improve the mechanical properties.

At the opposite extreme of behavior, hot-pressed silicon nitride exhibited delayed failure during the entire course of exposure for 1000 hours. Specimens that survived the 1000 hours exposure, however, were significantly stronger than those that had not been exposed to 1200 °C. Studies on specimens that were intentionally flawed by the use of a hardness indentation to form surface cracks indicate that crack healing occurs as a result of high-temperature exposure, so that the delayed failure that was observed cannot be attributed to machining damage, or to other flaws that were originally present in the specimen surface. Delayed failure was probably due to flaws that were generated as a consequence of high-temperature exposure. These results suggest that any theory of reliability developed to explain the high-temperature behavior of structural ceramics must take into account flaw generation, flaw healing, and crack growth.

Based on these experimental results, a theory of lifetime prediction has been developed for structural ceramics. The theory was presented at the Sixth AMMRC Materials and Technology Conference, "Ceramics for High Performance Applications--III" held at Orcas Island, Washington, (proceedings available as an NBS report, NBSIR 80-2024, May 1980). The theory accounts for the combined processes of flaw healing, pit formation, and subcritical crack growth. The theory independently evaluates these three processes and then determines the relative contribution of each of these processes to the total failure time. Conditions are established for proof testing of as-received components. Because of the occurrence of pit formation in hot-pressed silicon nitride, a maximum value for the proof-test load is established, above which proof testing does not contribute to component reliability. After long-term exposure, proof testing or nondestructive evaluation can be applied again if the flaw (pit) distribution has reached static equilibrium. If, however, the flaw distribution has reached a state of dynamic equilibrium, then statistical techniques must be applied for lifetime prediction. Assuming that the strength distribution of pits can be represented by a two-parameter Weibull distribution, statistics can be used for the combined failure modes of pit formation and crack growth. For these conditions, equations are developed for determining the total failure time.

Success of this theory requires detailed information on the modes of failure that may be operating in structural ceramics. Therefore, the assembly of experimental strength data on structural ceramics and the collection of microstructural information on these ceramics is vital for the development of a sound lifetime prediction capability. Since the modes of failure depend critically on the composition and type of ceramic being considered, data should be application specific; hence, one needs experimental data on a wide variety of ceramics exposed to temperatures and environments that reflect operating conditions. Our program has as its goal the collection of such data, and based on this data, the development of a viable lifetime prediction theory. If this program is successful, it will provide the basis for using ceramics in high temperature structural applications such as heat exchangers, turbines, and combusters.

The second part of the Division's program on structural ceramics is concerned with evaluating mechanisms of fracture at elevated temperatures. The specific objectives are to characterize high-temperature deformation and crack-growth and fracture behavior of structural ceramics that have potential application in coal-conversion systems. To measure crack velocity as a function of stress-intensity factor, an analysis of the four-point bend test was made that allowed the crack length, stress-intensity factor, and the crack velocity to be calculated from the points on a load-deflection curve. Hence, a notched, four-point bend test can be used to yield information on both fracture toughness and crack velocity as a function of stress intensity for a broad range of stress-intensity factors.

Materials include yttria-doped silicon nitride, several experimental compositions of silicon nitride with additions of garnet, and experimental grades of single-phase sialon (Si_5AlON_7) materials. Experimental materials are being supplied by Prof. Tien of the University of Michigan and by Dr. K. Kobayashi of the National Industrial Research Institute of Kyushu, Japan. Because of its high toughness and resistance to crack growth, the best grade of material examined so far was the yttria-doped Si_3N_4. The garnet-doped compositions of Si_3N_4 were found to exhibit severe oxidation at temperatures that exceeded 1300 °C, suggesting that these compositions cannot be used for structural applications at these temperatures. However, by noting the compositions that result in the highest toughness, crack-growth resistance, and oxidation resistance, a systematic approach can be used to develop the optimum composition for high-temperature structural design. The sialon compositions appear to oxidize rapidly at 1300 °C, probably as a result of migration of impurities from grain boundaries to the surface of the solid. Data obtained on this project are being reported to Dr. Tien and Dr. Kobayashi in order to lend direction to their fabrication efforts.

An important finding is that the fracture toughness of these materials at elevated temperatures is extremely sensitive to the loading rate. The fracture toughness of silicon nitride type materials increases dramatically at a critical value of the loading rate. The maximum toughness obtained as a function of loading rate depends on the test temperature. This effect is the result of the time-dependent nature of the creep strain field that forms around crack tips at elevated temperatures.

Bioceramic Materials: Another new and interesting application of ceramic materials is in the field of medicine. Certain types of ceramic materials (aluminum oxide, glass ceramics) are useful as structural components of prosthetic devices because they are biologically inert to the body environment and are relatively strong compared with bone. Consequently, these materials are being introduced into the body in several applications: total hip replacements, anchors for artificial teeth, and artificial knee joints. Given the tendency for ceramic materials to undergo stress-corrosion cracking due to water in the environment, there is concern over the ability of these materials to perform their function in the body environment for extended periods. Because of this concern, the Division has been conducting a study to determine the effect of microstructure on stress-corrosion cracking of aluminum oxide.

This year, experimental rigs to perform long-term delayed failure tests on biomaterials have been completed. The experimental setup consists of ten pneumatically loaded test fixtures. Specimens are held in tanks through which selected liquid environments are pumped from a heated container. A computer data acquisition and monitoring system was installed. Preliminary delayed failure data are being obtained in distilled water on Friedrichsfeld Al_2O_3, which is currently used as a biological implant material. When these studies have been completed, the fracture of these materials in a more realistic biological environment will be studied.

Materials for the NASA Gamma-Ray Observatory: A new project initiated during the past year involves the evaluation of the mechanical properties of alkali halides to be used as scintillation material for the NASA Gamma-Ray Observatory. CsI(Na) and NaI(Tl) are materials that scintillate; for this reason both are candidates for the crystal of NASA's Observatory. Because the mechanical properties of both candidates are largely unknown and alleged to be poor, achieving a flyable weight for the scintillator assembly is a primary design goal. Long-time deformation (creep) is the problem with CsI(Na); while low fracture toughness is expected to be the problem with a NaI(Tl) crystal assembly. Our goals are to determine the creep behavior of CsI(Na) and the effect of loading rate on the strength of NaI(Tl).

The fracture properties of NaI doped with Tl (Polysin) were evaluated to determine the fracture toughness of this material and to determine the possibility of stress-corrosion cracking as a cause of material failure. The critical-stress-intensity factor, K_{IC}, of the Polysin was evaluated in a low-humidity chamber using the double-cantilever-beam technique. Specimens were precracked to provide a starting crack for the fracture-toughness measurement. Values of K_{IC} (0.45 $MPa\cdot m^{1/2}$) were surprisingly high considering the low yield strength of this material and the lower values obtained on CaF (and on other alkali halides which are harder materials). Calculations of K_{IC} from flaw-size measurements on bend specimens were in good agreement with K_{IC} determined from the fracture-mechanics tests, suggesting that the fracture-mechanics value is the appropriate one for engineering purposes.

Stress-rate studies were conducted to determine the possibility of stress-corrosion cracking as a failure mechanism in Polysin. Tests were conducted in an environmental chamber in which the humidity could be controlled to dew point values as low as -43 °C. Accurate control of the humidity was necessary to prevent dissolution of the test specimens, which are highly hygroscopic. No effect of humidity was found in any of the tests conducted in this program. Surprisingly, plastic deformation affected the fracture properties of this material, causing the strength of specimens to increase slightly as the loading rate decreased.

In studies of the plastic properties of CsI doped with Na, the compressive strength was found to be approximately 0.79 MPa (1100 psi), larger than expected. However, the strength is strongly dependent on both the crystallographic orientation of the test sample and the annealing condition of the material.

Screening Tests for Ceramic Capacitors: The objective is the development of screening tests to assess the performance and expected lifetime of ceramic capacitors. Studies include the use of ultrasonic signals combined with sophisticated computer-analysis techniques as a means of detecting delaminations and cracks in capacitors, characterization of the microstructure of the ceramic capacitors and measurement of the susceptibility of the ceramic material in the capacitor to strength degradation resulting from internal stresses and subcritical crack growth.

The importance of this project rests on the use of these capacitors in critical military applications that require high functional reliability, so that the mechanical and electrical reliability should be ensured to the highest technically achievable levels. Recent experience indicates that the chance of capacitor malfunction in military hardware is sufficiently high as to cause real concern to DOD. Symptoms of malfunction (dielectric breakdown of the capacitor) often occur after the capacitors have been installed in components, which results in expensive repair operations that add significantly to the cost of the military hardware. Furthermore, since malfunctions often occur some time after installation, the reliability of operating systems may suffer as a result of capacitor malfunction. To alleviate these problems, research is being conducted to develop a better understanding of the causes of failure and to develop techniques to screen out defective capacitors.

During the past year, stress-rate tests were conducted on capacitor materials in air and synthetic sea water. The strength curves suggest a change in crack-growth mechanism in sea water at the highest loading rates.

The critical stress intensity factor, K_{IC}, was measured using precracked double-cantilever-beam specimens. The value obtained for K_{IC}, 0.8 $MPa \cdot m^{1/2}$, indicated a rather low resistance of the capacitor material to fracture. Although the value is low compared to other types of ceramics, such as Al_2O_3, it was consistent with values obtained on fine-grained $BaTiO_3$, a material commonly used for ceramic capacitors.

TEM studies were conducted on both neodymium and barium-titanate capacitors to reveal their microstructure. Although considerable difficulty was experienced in sectioning the capacitors for structural examination because of the tendency of these capacitors to fail at the metallic-ceramic interface, the technique of specimen preparation was mastered, and the structure was examined. The grain size varied from less than 1 μm to 10^5 μm and most grains contained a complex, three-dimensional domain structure, usually located near the center of the grain. Some compositions (neodymium titanate) also appeared to contain glass mixed in with the crystalline structure. Cracks appeared to propagate in a planar fashion and were not observed to interact strongly either with grain boundaries, or with the grains that were randomly oriented in the capacitor. A low resistance of the ceramic structure to crack propagation is suggested and is consistent with the low values of K_{IC}.

Refractories for MHD Applications: Refractory materials are used for MHD air preheaters. The high-temperature plasma (2400-2700 °C) necessary for operable and economically attractive open-cycle MHD power generation is achievable through the combustion of fossil fuels using air preheated to about 1500 °C. Such temperatures require the operation of regenerative heaters at temperatures as high as 1650 °C; the heaters require refractory materials that are capable of maintaining their mechanical integrity at this extreme temperature. Creep resistance is one of the primary properties that will determine the ability of refractories to perform adequately as components in regenerative heaters. Although several types of commercial refractory bricks have been selected to serve in this application, creep data on these materials are not available at temperatures exceeding 1500 °C. The objective is to obtain the necessary data on the high-temperature compressive creep of the refractories being considered for use in MHD air preheaters and to rank the proposed refractories in terms of their creep resistance at the service temperature of 1400 to 1650 °C.

A twelve-station creep apparatus has been designed and constructed for multiple creep experiments at temperatures as high as 1650 °C in air. The facility uses the pneumatic loading fixtures described elsewhere in this report. With this apparatus, specimens will be tested under static load for times up to 1000 hours at constant temperature, and with temperatures cycling between 1400 °C and 1600 °C. Samples of refractories used in the Montana State University air preheater apparatus were tested in compression at constant load and at constant loading rate at temperatures of 1400, 1500, and 1600 °C. Compressive creep specimens having a reduced cross-section were made from cores of (1) a chrome-spinel refractory, (2) a magnesia spinel refractory containing excess MgO, and (3) a fused-cast, sodium-doped alumina refractory. The dimensional stability of each material was measured for samples heated 24 hours at 1400, 1500, and 1600 °C. Changes in composition and phase were determined from x-ray powder diffraction patterns.

Friction and Wear of Ceramics
Subtask 4 of Task 12122

S. M. Wiederhorn, B. J. Hockey, E. R. Fuller, Jr., D. E. Roberts, R. S. Polvani

Friction and wear are important phenomena that determine the cost and reliability of precision-ground ceramic parts. Since machining often accounts for 90 percent of the cost of these parts, a considerable reduction in cost may be achieved by improving the machining process. Furthermore, since machining and erosion leave residual damage that reduces the strength of ceramic components, an understanding of these processes may lead to improvement in their strength. To achieve these ends, this project has been initiated to study the friction, wear, and erosion resistance of commercially important ceramic materials.

During the past year, work on the erosive wear of ceramic materials was directed toward: (1) completing our collection of data on the wear of aluminum oxide and silicon nitride, (2) studying the effect of grain size on wear, (3) clarifying the microstructure of impact craters in hot-pressed silicon nitride and fine-grain aluminum oxide, and (4) evaluating the dynamic hardness of ceramic materials.

Erosion Measurements: To complete our erosion data on ceramic materials, the erosion rate of hot-pressed silicon nitride and a new grade of hot-pressed aluminum oxide was measured using 150-μm silicon carbide particles at room temperature. The results on these materials were consistent with those obtained earlier.

The erosion rate of aluminum oxide is being measured as a function of grain size. Starting with fine grain aluminum oxide (2-3 μm) billets, specimens are being prepared with grain sizes ranging from 3 to 30 μm. These specimens will be used to determine the presence of a transition in the erosion rate (similar to that observed for K_{IC}) as the grain size increases.

Microscopy Studies: SEM and TEM were used to examine damage in the vicinity of hardness indentations placed in hot-pressed silicon nitride, and hot-pressed aluminum oxide. The effect of the fine grain size (2 μm) of both of these materials was readily apparent by examining the indented area with TEM. In contrast to observations on sapphire, or large grain size (~ 30 μm) sintered alunimum oxide, dislocation motion and crack motion are restrained by the presence of the grain boundaries. Cracking in the fine-grain (~ 2 μm), hot-pressed aluminum oxide was considerably less than that in the coarse-grain (30 μm) sintered material. In the hot-pressed silicon nitride, no cracks were observed when the indented regions were examined by SEM. However, as specimens were thinned for study, by TEM, cracks were observed to propagate from the indented regions. These observations support our finding that fine-grained ceramic materials wear much more slowly than coarse-grained materials.

Dynamic Hardness Measurements: Because of the importance of hardness to the nucleation of cracks during erosion, an attempt is being made to measure the dynamic hardness of ceramic materials. Two approaches were taken to obtain estimates of the dynamic hardness. The first was directed at the characterization of acoustic signals generated during impact, so that an impact-load, time profile could be obtained for real-time impact situations. The impact apparatus has been constructed, and the equipment is being coupled to a computer so that the impact data can be analyzed efficiently. Experiments will be conducted on large plates of soda-lime silica glass to obtain a reasonably accurate picture of the types of forces that are generated during solid-particle erosion.

The second method of measuring the dynamic hardness is based on the use of an electrically driven hardness indenter to apply loads to specimens for durations of about 1 ms. An apparatus of this type was built by Gunasekera and Holloway in 1973 to measure the dynamic hardness of glass. An electromagnetic driver capable of applying loads in times of less than 0.1 ms has been obtained. The load will be measured with a high-speed piezoelectric load cell. Displacements during indentation will be made with an eddy-current sensing device so that the entire load-displacement curve can be obtained for a single indentation. When completed, this equipment will represent a considerable advance over the apparatus used by Gunasekera and Holloway, who did not use a displacement device, and who depended on measurements of field current to determine the load on the sample. We hope to use the equipment to measure the dynamic hardness of a range of ceramic and metallic materials.

Microstructure of Ceramics
Subtask 5 of Task 12122

B. J. Hockey, N. J. Tighe

The objective is to investigate the relation between structural and mechanical properties of ceramic materials. Techniques of high-resolution TEM and SEM are developed and applied to study deformation, fracture and wear processes in hard materials.

During the past year, work was directed toward: (1) understanding the microstructure of ceramic capacitors, (2) elucidating mechanisms of erosion in brittle materials, and (3) clarifying the causes of strength degradation at elevated temperatures in non-oxide ceramics. Work on ceramic capacitors is discussed above in this report. In this section, studies of strength degradation mechanisms in non-oxide ceramics will be reviewed.

The structural stability of ceramics such as Si_3N_4 and SiC, which are intended for high-temperature turbine applications, depends on chemical reactions that occur between these materials and oxygen at elevated temperatures. Although these materials have excellent mechanical properties at room temperature their properties are often degraded by these reactions. Usually minor chemical components of the ceramic are the main cause for substantial losses in strength. In hot-pressed Si_3N_4

doped with MgO (as a sintering aid) for example, pit formation results in a strength loss of about 50 percent of the room temperature strength when the ceramic is exposed to temperatures exceeding 1200 °C. A second grade of hot-pressed Si_3N_4 that is doped with Y_2O_3 as a sintering aid is stable at temperatures exceeding 1200 °C, but disintegrates at temperatures of 800 to 1000 °C. Because this adverse behavior is caused by minor phases present in the ceramic, the electron microscope is an ideal tool for studying mechanisms of strength degradation.

The effect of catastrophic oxidation on the strength of hot-pressed Si_3N_4 doped with 10 percent Y_2O_3 was studied by high-voltage microscopy using an environmental chamber that could be operated at 750 °C. Studies were conducted at Case Western Reserve University in collaboration with Prof. A. H. Heuer. Specimens from a billet that reacted catastrophically with air at 750 °C were heated to this temperature in 40 torr of O_2. Under these conditions oxide platelets consisting of SiO_2 and Si_2N_2O were seen to nucleate on the surfaces of the Si_3N_4 grains, around holes and at yttria phases located at grain boundary junctions. After a few minutes of heating, cracks appeared along some of the grain boundaries demonstrating that large strains are associated with the oxidation, eventually resulting in a loss of grain-boundary integrity. These results suggest that the hot-pressed Si_3N_4 can be improved by chemical modification of the grain-boundary phases, which are the nucleation sites for oxidation.

Pit formation in MgO doped, hot-pressed Si_3N_4 was studied using a high-resolution, scanning, transmission electron microscope (STEM) at the Massachusetts Institute of Technology, and an SEM at NBS. An SEM examination of specimens exposed to 1200 °C for 100 hours indicated that the pitted area of these materials always contained a high concentration of iron. Examination of thinned sections of this material with the STEM indicated that the iron was always associated with tungsten inclusion contained within the solid and was not present in the test of the matrix. The association of iron with the pits suggests that pit formation in hot-pressed silicon nitride is caused by the presence of tungsten inclusions in the material. Since tungsten glasses have a low melting range relative to silica glass, oxidation of tungsten inclusions in the Si_3N_4 matrix forms a low-viscosity glass that enhances oxidation in the vicinity of the inclusion. In this way, pit formation occurs in the neighborhood of the inclusions. Mechanisms such as this have been suggested in the literature, and are supported by these microstructural findings.

<u>Engineering Evaluation of Composites</u>
<u>Subtask 6 of Task 12122</u>

M. B. Kasen, R. E. Schramm, B. A. Beck, R. D. Kriz

NBS, as a cosponsor of the International Cryogenic Materials Conference (ICMC), was instrumental in organizing an international topical conference on Nonmetallic Materials and Composites at Low Temperatures in Munich, Germany, during 1978. This Conference and its published proceedings served as a focus for addressing the problems of polymer performance at cryogenic temperatures combining both technology and science. The conference defined pressing research needs such as: (1) development of improved polymers for low-temperature use, especially those with improved toughness and lower notch sensitivity; (2) standardization of composite and polymer systems leading to reduced cryogenic variability and forming a basis for systematic materials development; and (3) improving the understanding of radiation resistance of polymers at 4 K, leading to the development of improved materials suitable for use in magnetic-fusion-energy reactor systems. A second session of this topical conference was held in Geneva, Switzerland, during August 1980. A paper emphasizing the need for increased standardization of composite materials was presented, reflecting a continued NBS role in this area.

The composite program during the past year saw the publication of a final report to the USAF on the properties and applications of advanced composites for the construction of prototype lightweight, airborne super-conducting-magnet systems. This work included a comprehensive update of the 1975 reviews addressing the effect of cryogenic temperatures on the performance of composite laminates. This will also be published separately in the literature. Also, an extensive tutorial review of composite-materials technology as applied to the cryogenic range was completed as a chapter in a forthcoming book entitled "Materials at Low Temperatures."

Research activities during the past year concentrated on the failure modes of composite laminates, emphasizing the role played by cryogenic temperatures. One effort undertook to develop the analytical base and techniques of failure analysis for fabric-reinforced nonmetallic composites tested under compression in the 295 to 4 K temperature range. The influence of constituent behavior and properties as an additional and integral part of the failure analysis is primary to an analytical interpretation of compressive fracture for such materials. There is presently a dearth of information concerning a systematic analytical treatment of room and cryogenic temperature behavior in glass-fabric reinforced composites. These materials to date have been considered too complex to be represented by analytical models. This study is specifically directed toward the fracture analysis of a G-10CR cryogenic-grade laminate. The information derived from such studies can provide a base that can be expanded and used for improved testing techniques for predicting behavioral and property patterns for fabric-reinforced nonmetallics at normal and low temperatures.

A fundamental assessment of the effect of cryogenic temperatures on the initial states of failure in graphite-epoxy materials was begun as part of a postdoctoral research program. This work examines the interrelationship between moisture and temperature on the damage accumulation in angle-ply laminates subjected to tensile loading. The object is to determine quantitatively how moisture and temperature affect the residual-stress state of individual layers of the laminate and to correlate these data with damage accumulation at the free laminate edge. An essential step in this program is the establishment of finite element analytical models to predict the laminate-edge stress state. The work will make a significant contribution to predicting damage accumulation in composite materials. The concept of a characteristic damage state for composites inherent in this approach is essential for the implementation of fracture-mechanics principles to composite materials.

NBS has continued cooperative work with the U.S. laminating industry to refine the common specifications for the CR grade of glass-fabric-reinforced laminates. The possibility of adding a random-mat glass-reinforced laminate and a uniaxial glass-reinforced laminate to the list of CR-grade products has been explored. Special emphasis has been placed on development of standardized grades for service under irradiation at 4 K. As part of a DOE program concerned with irradiation effects on composite electrical insulators in superconductivity magnets, NBS has obtained materials irradiated at Oak Ridge National Laboratory and has begun a study to correlate the molecular-level damage (measured in the Polymer Science and Standards Division) with property degradation. We have continued our interaction with the U.S. laminating industry to ensure that future radiation test materials are well controlled and amenable to fabrication as standard CR grades, should results warrant this approach.

ELASTIC-PLASTIC FRACTURE MECHANICS
Task 12123

Safety and durability are primary considerations in the design and construction of engineering structures. Sophisticated methods to assess structural safety and durability have been developed on the basis of linear-elastic fracture mechanics. These analytical methods are apppli-cable to the high-strength alloys used for aerospace vehicles and to the heavy-section steels used for nuclear pressure vessels. Unfortunately, the methods of linear-elastic fracture mechanics do not apply to a wide range of metal structures, including bridges, pressure vessels, ships, offshore structures, and pipelines. In these applications, the materials of construction (steels and aluminum alloys are typical) are highly plastic (nonlinear) before fracture. Consequently, linear-elastic methods do not apply and the assessments of structural safety and durability are based on empirical methods and prior experience. Although current methods usually provide a reasonable record of structural safety, improved efficiency and productivity could be achieved if more rational methods were used to establish material-toughness requirements allowable stress levels, minimum service temperatures, and weld-quality standards. The objective of this task is to contribute to the scientific basis (i.e., elastic-plastic fracture mechanics) for developing fracture-prevention procedures applicable to materials that exhibit extensive plasticity before fracture.

The Fracture and Deformation Division program in elastic-plastic fracture mechanics consists of five subtasks:

1. J-integral and crack-tip-opening-displacement evaluations are used to characterize the fracture resistance of structural alloys and determine the driving force for fracture under elastic-plastic conditions.

2. Fitness-for-service criteria are being used to evaluate the significance of defects, particularly in weldments, on the basis of plastic-strain cycling fatigue tests, elastic-plastic fracture-mechanics concepts, and nondestructive evaluation procedures.

3. The elastic-plastic fracture properties of alloys and weld-ments used for low-temperature applications, such as LNG tankage and superconducting-magnet structures, are being evaluated.

4. Elastic-deformation phenomena are being studied to contribute to our understanding of the fundamental basis of strength.

5. Test methods and standards are being developed for the charac-terization of the fracture behavior of materials.

<u>J-Integral and Crack-Tip-Opening-Displacement (CTOD) Evaluations</u>
Subtask 1 of Task 12123

D. T. Read, R. W. Cheng, R. deWit, J. G. Early, H. I. McHenry

The J-integral and the CTOD are simply related characterizations of the elastic-plastic field in the vicinity of the crack tip. The value of the J-integral for any contour surrounding the crack tip has been shown experimentally to be a criterion for the onset of crack extension. Experimental methods have been developed to determine the critical value of J, J_{IC}, and of CTOD, Si, which are measures of the plane-strain fracture toughness. The Fracture and Deformation Division is conducting research using the J-integral and CTOD methods to characterize the fracture toughness of structural alloys, to measure the driving force for fracture under elastic-plastic loading conditions, and to conduct analytical studies to evaluate the influence of geometric configuration and stress-strain characteristics.

The Division is conducting a program to develop a J-integral design curve along the lines proposed in the Draft British Standards Rules for Derivation of Acceptance Levels for Defects in Fusion Welded Joints. The program involves the experimental determination of the relationships of the J-integral fracture toughness, the applied strain, and the defect size. Initial tests involved tensile panels of ship steel with edge cracks, center cracks, surface cracks, and cracks adjacent to stress concentrations. The influence of residual stress on the design curve will be assessed using wide-plate test specimens fabricated by the Navy and tested in the NBS large-scale test facility. Results to date have led to the development of an extended elastic-perfectly-plastic model applicable to through cracks in open areas of tensile panels. Stress concentration effects can be accounted for by a uniform strain model and the Neuber strain concentration. Future work will emphasize surface-flaw modeling and tests on weldments.

Finite-element-analysis studies are being conducted to complement the experimental program to develop a J-integral design curve. The analytical work is being performed by Professor Robert Dodds of the University of Kansas under contract to NBS. Work in progress is directed toward developing relationships between the J-integral and nominal strain for cracks adjacent to stress concentrations such as holes and elliptical cutouts. The objective of the finite element analyses is to demonstrate that the experimental results can be numerically simulated and to generalize the experimental results to a variety of stress concentrations in a manner that is more efficient than actual experiments.

A study of fracture-characterizing parameters is being conducted for NBS by Dr. M. G. Dawes of the Welding Institute, Abington, England. Dr. Dawes is performing the research at the Boulder laboratories thereby permitting the improvement of our experimental capabilities, particularly in the area of CTOD testing. The experimental program addresses the influence of plastic constraint on observed fracture behavior. Especially large errors can be introduced by present experimental measurements of critical J-integral or CTOD values for the onset of cleavage fracture, which often show large variations due to differences in crack-tip-region plastic constraint (CPC) between laboratory test specimens and cracks in structures. For example, the critical values of J or CTOD obtained in deeply notched single edge-notched bend (SENB) specimens may grossly underestimate the toughness associated with identical material at the tips of smaller SENB specimens or shallow surface cracks in large structures. Although published research indicates a growing awareness of these situations, there appears to be no generally acceptable method available at this time for quantifying the magnitude of the crack-tip-region plastic constraint. The approach being taken is to obtain a comprehensive set of elastic-plastic fracture data (both J and CTOD) on a C-Mn steel for specimen designs having a wide range of plastic constraint. These data will demonstrate geometry dependence and establish an empirical basis for developing a parameter to characterize the influence of plastic constraint.

A theoretical study of cleavage fracture is being conducted to complement the empirical studies. The investigation is being conducted for NBS by Ohio State University under the direction of Dr. Ing-Hour Lin. Dr. Lin is developing a model that is an extension of the work of Ritchie, Rice, and Knott. It uses the strain-field solutions of Hutchinson to predict stress-state effects on the brittle-to-ductile fracture-mode transition. The data developed by Dawes will be used to evaluate the resulting theoretical predictions. In addition to plastic constraint effects, metallurgical factors are being investigated, particularly grain-size effects, and statistical treatments of the fracture-mode transition.

Fitness-for-Service
Subtask 2 of Task 12123

Y.-W. Cheng, C. M. Fortunko, E. L. Brown, M. B. Kasen, H. I. McHenry, J. H. Smith, J. G. Early, R. deWit, G. E. Hicho

A program is being conducted to establish weld-quality requirements for the Alaska Natural Gas Transportation System (ANGTS). Analytical studies involve modeling of the significance of defects using methods comparable to those used for the trans-Alaska pipeline assessment conducted previously. Experimental studies involve the measurement of crack-mount opening-displacement (CMOD) as a function of remote strain for tensile panels with surface flaws. These specimens are also instrumented with strain and remote displacement gauges to evaluate the J-integral for two-diemnsional contours (two paths) where the surface flaw is treated as an edge crack in one case and as a through-thickness center crack in the other case. The results of these experimental and analytical studies will be used to assess the validity of the critical COD models used in the trans-Alaska oil pipeline. These models have been reassessed and their sensitivities to applied stress and material tensile flow properties compared and evaluated. In the case that the critical COD model does not represent the experimental observations, work will follow on the development of an improved analytical model.

Testing has been completed to determine the fracture toughness of girth welds from API-grade X-65 line pipe. Metallographic analyses were conducted, and fracture toughness measurements were made using the multiple-specimen procedure to determine J_{IC} for the welds. Research is continuing to characterize weld defects, particularly slag porosity, in girth welds from gas-transmission pipelines. Radiographs were made of these welds and were analyzed to characterize the length and width of the defects. These results will be correlated with the results of metallographic analysis to assess the reliability of methods for characterizing the weld defects. NBS is working closely with the Canadian gas-pipeline materials research at Alberta Gas Trunkline Company and the Canadian Welding Institute, the Northwest Pipeline Company, the Welding Research Council, the American Pipeline Institute standards committee, and Battelle Memorial Institute in this program.

A major effort has been started to develop ultrasonic inspection methods for determining the depth of flaws in weldments. Initial objectives relate to the fitness-for-service standards being developed for the ANGTS system. An NDE laboratory has been built, equipped, and staffed during the past year to conduct the NDE investigations. Initial emphasis has been on the development of electromagnetic acoustic transducers (EMATS) to size defects. The EMATS excite horizontal shear (SH) waves in the weldments that are reflected by flaws in proportion to their depth. A prototype EMAT system has been designed, built, calibrated, and evaluated for inspecting pipeline girth welds. The results to date indicate that the EMATS have a sufficient signal-to-noise ratio to effectively size flaws in pipeline girth welds. The emphasis of future research will be on developing the physical basis through parametric studies to permit industry to build a system for field applications.

A new program has been initiated to evaluate the suitability of high-strength low-alloy (HSLA) steels for transportation applications. HSLA steels are a new class of materials that use microalloying, inclusion shape control, and controlled processing to significantly improve the strength, toughness, and weldability of conventional steels. Their application in transportation systems is currently limited by the lack of improved fatigue strength when welded. Despite improved strength and toughness, the durability of HSLA steel weldments is essentially the same as conventional steels. The reasons for the relatively poor performance in fatigue are not clearly understood. Stress concentration effects, residual stress, and metallurgical deterioration have been suggested as possible causes. The relative importance of these contributing factors is being evaluated to improve fatigue strength. The experimental approach is to metallurgically examine fatigue-tested samples of HSLA steels with and without welding, stress concentrations, and residual stress. Ford Motor Company, General Motors Corporation, and the HSLA steel suppliers are collaborating with NBS on this program.

A conference entitled "Fitness-for-Service of Welded Structures" was cosponsored by NBS and the American Welding Society (AWS). It was held in Indianapolis, Indiana, in May 1980. Over 150 engineers and researchers attended and rated the conference as highly informative and beneficial. The conference featured twelve invited speakers covering the role of design, analysis, materials, selection, fabrication controls, and quality assurance in the implementation of fitness-for-service standards. Experience with fitness-for-service standards for steel weldments, nuclear pressure vessels, and pipelines was reviewed by leading authorities in these fields.

Low-Temperature Properties
Subtask 3 of Task 12123

R. P. Reed, R. L. Tobler, H. I. McHenry, J. M. Arvidson, R. E. Schramm

A major developing technology is the use of superconducting magnets in energy applications. High magnetic fields are required for fusion-plasma and MHD-plasma confinement and guidance. Superconducting machinery, under prototype development, provides the potential for better performance coupled with lighter weight and reduced space requirements. Power transmission via superconducting underground cables is under intensive development. Energy storage, using large superconducting rings, is being considered. In all applications, the magnet or superconductor, with appropriate structural supports, is expected to operate at liquid-helium temperature (4 K) up to 20 years.

Such emphasis on liquid-helium design and material use has led to large national materials programs, sponsored by DARPA and DOE and managed by our Division. These programs have produced a low-temperature materials handbook; mechanical, thermal, electrical, and magnetic characterization of economical structural alloys including austenitic stainless steels, aluminum alloys, and superalloys; an annual Low-Temperature Materials Workshop held each October in Vail, Colorado; and joint research programs between NBS and its subcontractors, which have included Battelle, Westinghouse, General Electric, Martin-Marietta, Teledyne-McKay, Alcoa, Armco, and Belfour-Stulen. Major research emphasis has been to characterize the austenitic stainless steels (AISI 304, 316, and 310 grades) and to develop reliable welding processes and filler metals for welding austenitic stainless steels for use at low temperatures. The development and characterization of low temperature composite insulator standards is discussed in the previous task.

Superconducting magnets are needed for both fusion and MHD applications to contain and direct the flow of the plasma. A major obstacle to the development of large superconducting magnets, to operate at -269 °C, is the requirement of strong, tough, and weldable alloys to restrain the large magnetic forces. We are developing and characterizing a new class of austenitic stainless steels for this application. Interstitial strengthening of a conventional austenitic Fe-Cr-Ni alloy is achieved by adding nitrogen and increased alloy formability and nitrogen solubility limits are achieved with the addition of manganese. We are studying the influence of nitrogen and manganese on the temperature dependence of the flow strength, activation energies and volume, martensitic transformations, fracture toughness, and fatigue-crack-growth rates from room temperature to -269 °C. Results indicate that the dependence of flow strength on nitrogen concentration increases dramatically at low temperatures. Nitrogen additions suppress both the body-centered-cubic and close-packed-hexagonal martensitic transformations. A linear relationship between fracture toughness (from J-integral measurements) and tensile yield strength at -269 °C was found. The temperature dependence of the flow strength is critically dependent on austenite stability; low austenite stability results in strain-induced martensite formation, which produces low flow strengths. An analytic expression has been developed relating flow strength to temperature in the absence of martensitic transformation for austenitic Fe-Cr-Ni alloys. Alloys containing controlled nitrogen and manganese concentration have been supplied by U.S. Steel and Armco Steel Corporations.

Fracture-mechanics evaluation of weldments continued. The fracture toughness of 316L welds at 4 K decreased in the following order: gas-t ungsten-arc, gas-metal-arc, and submerged-arc. An evaluation of 5083-aluminum-alloy weldments for liquid-helium service indicated remarkable consistency in toughness for welds provided by six industrial firms using the gas-metal-arc process.

The US/USSR scientific exchange program on Cryogenic Materials and Welds is being maintained by the National Science Foundation. A 20Cr-16Ni-6Mn-.2N stainless steel alloy weldment supplied by the Paton Institute was evaluated for use in superconducting magnets. The combination of strength and toughness in the submerged-arc welds of this alloy at 4 K is superior to any alloy previously evaluated and is comparable to expected values for the matching base plate. Thus, this alloy appears promising for liquid-helium service.

Elastic Deformation Phenomena
Subtask 4 of Task 12123

H. M. Ledbetter

Elastic constants provide fundamental information about solids to both the solid-state physicist, who wonders what holds solids together, and to the materials engineer, who wonders what tears them apart.

Our effort on solid-state elastic constants comprises three categories: (1) critical reviews of elastic-property data, (2) experiment, and (3) theory. Related theoretical studies on solid-solid phase transitions are also in progress.

Our critical reviews focus on materials of both scientific and technological importance: iron, nickel, copper, zinc, iron-nickel alloys (completed); copper-zinc alloys, aluminum (in progress) magnesium, titanium, and others (planned). Besides recommending "best" elastic constants, these reviews consider effects of variables such as temperature, pressure, alloying, magnetic field, and mechanical deformation, and identify suggested areas for further study. From both university and industrial laboratories, we have received considerable encouragement for more studies of these kinds.

Our experimental studies deal with metals, alloys, composites, and polymers; with single crystals and with polycrystals. Notable recent studies include: (1) the effects of interstitial carbon and nitrogen on the elastic constants of austenitic stainless steel 304, (2) elastic constants of a wide range of commercial austenitic stainless steels, (3) accurate measurements (for the first time) of polycrystalline copper's low-temperature elastic constants, (4) determination of Young's modulus and internal friction at low temperatures for glass-epoxy composites and for the epoxy resins, and (5) orientation dependence of Young's modulus and damping in glass-cloth-epoxy composites. We are developing two new (for NBS) experimental capabilities: a forced-vibration system for low-frequencies (1-100 Hz) and a continuous-wave, standing-wave method for high-frequencies (1-10 MHz). The first system is being used to study polymers and composites (high damping materials). The second system is being used initially to investigate cracks in ceramic capacitors used in inertial-guidance systems.

Our theoretical efforts focus on three principal problems: (1) relationships between elastic constants and other physical properties, particularly the Debye characteristic temperature; (2) relationships between physical properties of single crystals and polycrystals, that is, the tensor-averaging problem; and (3) elastic constants and interatomic potentials. On the latter problem, collaborating with T. Suzuki (Tsukuha University), we recently calculated the elastic constants of the alkali metals using pseudopotentials and related these constants to the phase-transition behavior of the metals. From these calculations is emerging an exciting new concept for low-temperature solid-state nucleation of the new phase. Basically, the traditional surface-energy-term approach, which fails to predict reaction rates, is replaced by a lattice-deformation-energy term that might. These calculations also provide new insights into the relative phase stability of sodium, which exhibits three crystal structures. On the single-crystal: polycrystal elastic-constants problem, much of our work is now done in collaboration with the theoretical group of Prof. E. Kröner at the University of Stuttgart. These studies are summarized in a foreign trip report by H. Ledbetter (August 1980). In terms of elastic-constant; physical-property relations, we would like to extend our preliminary studies on bcc transition metals where the superconducting transition temperature, T_c, relates to the Cauchy discrepancy, C_{12}-C_{44}. Collaborating with Prof. S. K. Datta (University of Colorado), we have carried out perhaps the most thorough comparison to date between theory and observation for the elastic constants of a uniaxially reinforced metal-matrix composite.

<u>Test Methods and Standards</u>
Subtask 5 of Task 12133

B. W. Christ, R. deWit, J. G. Early, G. E. Hicho, C. G. Interrante, J. H. Smith, W. A. Willard

The development of test methods and standards for characterizing and specifying materials is a major activity of the Fracture and Deformation Division. The need for specific test methods and materials standards is often initially identified through our failure-avoidance efforts conducted for other Government agencies. The current activities are summarized as follows:

Development of Standard Reference Materials (SRM): Under sponsorship of the NBS Office of Standard Reference Materials, a series of SRM's has been developed for calibrating instruments used to determine the level of retained austenite in ferrous alloys. Samples to be sold as the SRM are prepared from metal powders of austenite and ferrite phase materials and consolidated by powder metallurgical techniques. These samples are then calibrated by x-ray and metallographic analysis and certified for sale. During the past year, a series of austenite SRM samples containing 15 percent austenite and a series of specimens containing five percent austenite have been prepared, calibrated, and will be offered for sale by the Office of Standard Reference Materials. To complete this series, SRM's containing 2.5 percent and 30 percent austenite will be prepared during the coming year. The availability of these standard reference materials is essential for the accurate calibration of instruments to measure the retained austenite in materials purchased by specifications which place a maximum on retained austenite.

Standard Test Methods for Hydrogen Embrittlement Cracking: Hydrogen embrittlement cracking (HEC) is a significant cause of unexpected fracture in structures made from ferrous alloys. Reliable test methods to assess the susceptibility of ferrous alloys are required to reduce the incidence of HEC in ferrous alloys. An original test method to assess the thermal diffusivity of hydrogen in metals has been developed by J. G. Early. This test method is required to assess the tendency for hydrogen to be absorbed and cause embrittlement in ferrous metals. This test method has been calibrated with palladium and will be used to determine the thermal diffusivity of hydrogen in several ferrous alloys.

A project has been initiated to use neutron-inelastic scattering to determine the effect of local stress fields on the local atomic interaction between hydrogen and iron atoms in specimens of steel under stress. This project will be carried out cooperatively with the NBS Reactor Radiation Division. Results of this highly innovative approach will lead to a much clearer understanding of the mechanism for the interaction of stress and hydrogen in causing embrittlement of steel.

Development of Test Methods for Assuring the Safety of Pressure Vessels: Research is continuing on programs for the Office of Hazardous Materials Regulations (OHMR) to develop appropriate test methods and provide the basis for developing standards for the safe shipment of hazardous materials in portable pressure vessels. Work has been completed on assessing the validity of various mechanical properties tests used for acceptance of homogeneous seamless steel cylinders. The results of this program will permit a fair and equitable comparison to be made between cylinders manufactured in the U.S. and in foreign countries and to ensure the same level of safety for all classes of cylinders. A program has been initiated to assess the fracture toughness of various cylinders and to assess the need for requiring fracture toughness requirements on materials for use in seamless steel vessels.

An extensive program was initiated this year to develop reliable test methods and acceptance standards for the use of composite pressure vessels for the transportation of hazardous materials. At present, attention is focused on cylinders made by overwrapping aluminum cylinders with fiberglass reinforced plastic and Kevlav. Tests are being assessed and developed for assessing the safety of these vessels in ambient environments, high temperature environments, and in acqueous environments. The results of these tests will be used by OHMR to develop specifications for allowing wide scale use of composite cylinders.

Development of Test Method for Elevated Temperature Stress--Corrosion
Work has been completed, under Department of Energy sponsorship, on the development of a test method for assessing the susceptibility of materials to stress-corrosion cracking at elevated temperature. This test method permits the use of a thermally compensated, pre-cracked test specimen for determining crack growth rate *in situ* in field tests in aggressive environments.

Analysis of Shipbuilding Materials Standards: Under sponsorship of the Coast Guard, a program was initiated this year with the principal effort in the analysis of American, German, and Japanese materials standards and their equivalency or lack of equivalency. Considerable progress has been made on the initial group of 60 specifications. The results of this study will be submitted for a Symposium on Shipbuilding Standards to be held in 1981 sponsored by ASTM and the Society of Naval Architects and Marine Engineers.

Development of Standards for Resource Recovery: In cooperation with the ASTM Committee E-38 on Resource Recovery standards E702, "Standard Specification for Municipal Ferrous Scrap," and E701, "Standard Methods of Tests for Municipal Ferrous Scrap," were developed and approved. J. G. Early of the Fracture and Deformation Division served as Secretary of the E-38 Committee and as a principal author of these standards. These standards are essential to permit the economical recycling of ferrous materials in municipal waste. A chapter entitled "Recycling Ferrous Scrap" is in preparation and will be published in the 3rd Edition of the "Encyclopedia of Chemical Technology" early in 1981.

ASTM Subcommittee E24.03 - Alternative Fracture Test Methods: Chairmanship of this subcommittee involves fostering fracture test methods that use simple tests of notched or precracked specimens not based upon fracture mechanics analysis. These alternative test methods are frequently used in fracture control, especially for metals with high toughness. They include the Precracked Charpy and the Dynamic Test Test Methods. For the precracked Charpy test, separate methods are being developed for impact testing and for slow-bend testing. The forerunner to these developments is an extensive analysis conducted at NBS on "The Significance of Precracking Variables for Slow-Bend Charpy Tests." Future activities will include participation in round-robin activities on these test methods.

Terminology: Our work in the area of terminology is concerned mainly with terminology for fracture testing and it includes staff participation in an international committee, ISO TC164/WG on Terminology for Mechanical Testing, as well as in several national committees, the ASTM Committee on Terminology, ASTM Subcommittee E-24.05 on Terminology for Fracture Testing, and the ASM Committee on Definitions of Metallurgical Terms. The Chairman and Secretary of SC E-24.05 serve in a diversified set of roles to facilitate and coordinate the development of terminology within the many task groups of eight subcommittees of Committee E-24. This terminology includes development definitions, descriptions of terms, recommended symbols, abbreviations, and units, as well as guidelines for use of the SI Metric Practice. Another aspect of this work is the coordination of the terminology of E-24 with that of other ASTM committees and other national and international bodies concerned with terminology for fracture testing.

ASTM Task Group E-24.06.02 - Application of Fracture Analysis Methods: Membership in this task group involves participation in a predictive round-robin whose objective is to experimentally verify whether or not analytical methods currently in use can predict failure of complex structural components containing cracks from results of laboratory tests. The results of a great deal of analytical work done over the past year are now being coordinated by the Task Group.

ASTM Task Group E-10.02-C on Interpretation of Charpy Data: Membership in this task group involves participation in the development of a standard for Computer Analysis of Charpy Impact Test Data, and it has included the writing of an NBS Appendix for this proposed standard. The appendix is titled, "General Method for Computer Analysis of Charpy Impact Data."

Other Activities of the
Fracture and Deformation Division

Invited Talks

Energy Variations in Diffusive Cavity Growth
Fall Meeting of Basic Science and Nuclear Divisions, American Ceramic Society, New Orleans, Louisiana
T.-J. Chuang
October 1979

Energy Related Standards in Resource Recovery
USA Energy Self-Sufficiency Symposium, New Orleans, Louisiana
J. G. Early
January 1980

Deformation and Fracture Mechanism Maps with an Introduction to Crack Growth Mechanism Maps
Pennsylvania State University, Materials Science and Engineering Seminar
R. J. Fields
February 1980

Aspects of Subcritical Crack Growth in Organic Fluids
Glass Division, American Ceramic Society
Bedford Springs, Pennsylvania
S. W. Freiman
October 1979

Stress Corrosion of Ceramics
Case Western Reserve University, Cleveland, Ohio
S. W. Freiman
January 1980

Fractographic Analysis of Brittle Fracture
NASA Lewis Research Center, Cleveland, Ohio
S. W. Freiman
January 1980

Understanding and Prediction of Delayed Failure in Ceramics
Annual Meeting, Canadian Ceramic Society, Ottawa, Canada
S. W. Freiman
February 1980

Effect of Stress on Raman Spectra of Optical Fibers
Annual Meeting, American Ceramic Society, Chicago, Illinois
S. W. Freiman
April 1980

NBS Program
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
R. P. Reed
October 1979

US/USSR Exchange Program
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
R. P. Reed
October 1979

Fracture Energy of Si_3N_4
Annual Meeting, American Ceramic Society, Chicago, Illinois
R. R. Rice
April 1980

Effect of Alkali Ion Exchange on Crack Propagation in Glass
Glass Division, American Ceramic Society
Bedford Springs, Pennsylvania
C. J. Simmons
October 1979

Relation of Subcritical Crack Growth to Chemical Durability of Glasses in Aqueous Solutions
Annual Meeting, American Ceramic Society, Chicago, Illinois
C. J. Simmons
April 1980

Requirements for Failure Analysis Methodology
ASME Pressure Vessels and Piping Division Meeting, Foster-Wheeler Corporation, Livingston, New Jersey
J. H. Smith
December 1979

Fracture Mechanics Analysis to Determine Allowable Flaw Sizes in Girth Welds
DoT-NBS Pipeline Meeting, Boulder, Colorado
J. H. Smith
March 1980

Safety Factors in Fatigue Design: Arbitrary and Rational
ASME Symposium-Critical Materials and Lubrication Issues for Pressure Vessels, Piping, Pumps, and Valves, San Francisco, California
J. H. Smith
August 1980

Conditions for Lattice Trapping of Cracks: Normal and Anomalous Glass
American Ceramic Society, 82nd Annual Meeting, Chicago, Illinois
R. M. Thomson
April 1980

Effect of Oxidation on the Flaw Population in Si_3N_4 Compacts
American Ceramic Society, New Orleans, Louisiana
N. J. Tighe
October 1979

Corrosion and Stress Corrosion of Ceramics
Sandia Laboratories, Albuquerque, New Mexico
S. W. Freiman
May 1980

Determining Crack Growth Behavior from Delayed Failure Test
American Ceramic Society, 82nd Annual Meeting, Chicago, Illinois
E. R. Fuller, Jr.
April 1980

High-Temperature Double-Torsion Studies of Refractory Concretes
ASTM Symposium on Fracture Mechanics Methods for Ceramics, Rocks, and Concrete, Chicago, Illinois
E. R. Fuller, Jr.
June 1980

Fractographic Evaluation of Slow Bend Precracked Charpy Specimens
ASTM E24 Committee Meeting, Pittsburgh, Pennsylvania
G. E. Hicho
October 1979

Erosion of Ceramics by Solid Particle Impact
Army Research Office Workshop on "Mechanisms of Erosion in Hot Flowing Media," Fort Myers, Florida
B. J. Hockey
October 1979

Role of the Committee on Terminology in ASTM
Meeting of Subcommittee E9.06 on Statistical Aspects of Fatigue, Pittsburgh, Pennsylvania
C. G. Interrante
October 1979

A Review of COT Recommendations for ASTM Terminology
Meeting of Subcommittee E9108 on Fatigue under Cyclic Strain and Executive Subcommittee E9.90 on Fatigue, Pittsburgh, Pennsylvania
C. G. Interrante
October 1979

Terminology in ASTM
Meeting of ASTM Editorial Subcommittee B5.91 on Copper and Copper Alloys, Galt House, Louisville, Kentucky
C. G. Interrante
March 1980

Terminology in ASTM
Meeting of ASTM Subcommittee B9.01 on Nomenclature for Metal Powder and Metal Powder Products, Galt House, Louisville, Kentucky
C. G. Interrante
March 1980

Terminology in ASTM
Meeting of ASTM Subcommittee C8.06 on Nomenclature for Refractories, Galt House, Louisville, Kentucky
C. G. Interrante
March 1980

Fracture of Steel Plate Materials under Abusive Service Conditions
Mechanical Failures Prevention Group Symposium in Ground Transportation Systems, 31st Meeting, NBS, Gaithersburg, Maryland
C. G. Interrante
April 1980

Standardizing Nonmetallic Composite Materials for Cryogenic Applications
ICMC Conference on Nonmetallic Materials at Low Temperatures-II, Geneva, Switzerland
M. B. Kasen
August 1980

High Temperature, High Pressure, Fluid Handling Facility
Task Group on Geothermal Wells, Committee on Oil-Well Cements, American Petroleum Institute, Tulsa, Oklahoma
R. F. Krause, Jr.
December 1979

Strength Measurements of Cements Following Hydrothermal Exposures
Task Group on Geothermal Wells, Committee on Oil-Well Cements, American Petroleum Institute, San Antonio, Texas
R. F. Krause, Jr.
March 1980

Strength Measurements of Cements Following Simulated Geothermal Exposures
Task Group on Geothermal Wells, Committee on Oil-Well Cements, American Petroleum Institute Standardization Conference, Houston, Texas
R. F. Krause, Jr.
June 1980

Structural Alloys for Superconducting Magnet Systems
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania
H. I. McHenry
June 1980

Fractographic Analysis of Delayed Failure in Ceramics
ASTM Symposium on "Fractography and Materials Science," Williamsburg, Virginia
J. J. Mecholsky
November 1979

Direct Measurement of the J-Contour Integral
International Conference on Analytical and Experimental Fracture Mechanics, Rome, Italy
D. T. Read
June 1980

Deformation of CR-Spinel Refractory Brick
American Ceramic Society, Chicago, Illinois
N. J. Tighe
April 1980

Cryogenic Properties of Stainless Steel Welds
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
T. A. Whipple
October 1979

Cryogenic Properties of Stainless Steel Welds
AWS Meeting, Los Angeles, California
T. A. Whipple
April 1980

Proof Testing of Ceramics: Effect of Multiregion Crack Growth
American Ceramic Society, 32nd Pacific Coast Region Meeting, Seattle, Washington
S. M. Wiederhorn
October 1979

Micromechanisms of Crack Growth in Ceramics and Glasses in Corrosive Environments
Micromechanisms of Crack Growth Conference, Cambridge, England
S. M. Wiederhorn
March-April 1980

Effect of Region II Crack Growth on Proof Testing
American Ceramic Society, 82nd Annual Meeting, Chicago, Illinois
S. M. Wiederhorn
April 1980

Erosion of Ceramic Materials
Argonne National Laboratories, Chicago, Illinois
S. M. Wiederhorn
May 1980

Technical and Professional Committee Participation and Leadership

American Association for the Advancement of Science
S. W. Freiman, B. J. Hockey, and J. H. Smith, Members

American Ceramic Society
T. Chuang, R. J. Fields, S. W. Freiman, E. R. Fuller, Jr. (Chairman Elect of the Baltimore-Washington Chapter), B. J. Hockey, C. L. McDaniel, N. J. Tighe, and S. M. Wiederhorn, Members
Executive Committee
N. J. Tighe, Member
Forum Committee
N. J. Tighe, Member
Sosman Lecture Committee
N. J. Tighe, Member
Editorial Committee
S. M. Wiederhorn, Subchairman

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M. B. Kasen, Member
Definitions of Metallurgical Terms
C. G. Interrante, Member
Long-Range Planning Committee
C. G. Interrante, Chairman
Metals Information Publications Committee
J. H. Smith, Member

American Iron and Steel Institute
Task Force on Evaluation of Fracture Criteria for Ship Steels and Weldments
H. I. McHenry, Member

American National Standards Institute (ANSI)
Materials and Stresses Committee of the Pressure Piping Code, B31
H. I. McHenry, Member

American Petroleum Institute
Task Group on Cements for Geothermal Wells
E. R. Fuller, Jr., and R. F. Krause, Jr, Members

American Physical Society
R. C. Dobbyn, E. R. Fuller, Jr., R. deWit, and B. J. Hockey, Members

American Society for Metals (ASM)
B. W. Christ, T. Chuang, R. deWit, J. G. Early, R. J. Fields, G. E. Hicho, C. G. Interrante (Past Chairman, Washington Chapter), H. I. McHenry, R. S. Polvani, T. R. Shives, J. H. Smith, and N. J. Tighe, Members

American Society for Testing and Materials (ASTM)
R. deWit, R. C. Dobbyn, B. W. Christ, J. G. Early, R. J. Fields, S. W. Freiman, E. R. Fuller, Jr., G. E. Hicho, C. G. Interrante, M. B. Kasen, T. R. Shives, J. H. Smith, R. L. Tobler, and S. M. Wiederhorn, Members
Committee on Terminology (COT) of Committee on Standards
C. G. Interrante, Member
Committee C-21 Ceramic Whitewares
S. M. Wiederhorn, Member
Committee D30 Composite Materials
M. B. Kasen, Member
Subcommittee D30.05 High-Modulus Fibers and Their Composites
M. B. Kasen, Member
Committee E4 Metallography
R. J. Fields, Member
Subcommittee E9 Fatigue
R. J. Fields, Member
Subcommittee E9.01 Fatigue Research
R. C. Dobbyn, Member
Subcommittee E9.03 Fatigue of Composites
M. B. Kasen, Member
Subcommittee E10.02-A Computer Methods for Analysis of Charpy Data
C. G. Interrante, Member
Committee E24 Fracture Testing
B. W. Christ (Member of Executive Committee), R. deWit, R. J. Fields, E. R. Fuller, Jr., G. E. Hicho, C. G. Interrante (Member of Executive Committee), J. H. Smith, R. L. Tobler, and S. M. Wiederhorn, Members
Task Group E24.01.09 Elastic Fracture
R. L. Tobler, Member
Subcommittee E24.02 Fractography
G. E. Hicho, Vice Chairman
Subcommittee E24.03 Alternative Test Methods
B. W. Christ, Chairman

Task Group E24.03.03 Precracked Charpy Testing Methods
C. G. Interrante, Member
Subcommittee E24.05 on Terminology
C. G. Interrante, Chairman and R. deWit, Secretary
Task Group E24.06.02 Predictive Round Robin on Fracture
R. deWit, Member

Subcommittee E24.07 on Fracture of Non-Metals
S. W. Freiman, Chairman and E. R. Fuller, Jr., Member
Subcommittee E24.07.01 Fracture Toughness Testing of Concretes and Rocks
E. R. Fuller. Jr., Member
Subcommittee E24.07.02 Double-Torsion Technique
E. R. Fuller, Jr., Member Task Group E28.04.03 Verification of Alignment Under Tensile Load
B. W. Christ, Chairman
Subcommittee E38 Resource Recovery
J. G. Early, Secretary and Member of Executive Committee
Subcommittee E38.02 Ferrous Metals Resource Recovery
J. G. Early, Secretary
Joint ASTM-ASME-MPC Committee on Effect of Temperature on the Properties of Metals
R. P. Reed, Member and B. W. Christ, Guest Member representing NBS

American Society of Mechanical Engineers (ASME)
T. Chuang, R. deWit, R. C. Dobbyn, J. H. Smith, and N. J. Tighe, Members
Ceramics Committee
N. J. Tighe, Member
Gas Turbine Division
N. J. Tighe, Member
Joint Applied Mechanics Division and Materials Division Committee on Constitutive Equations
R. deWit, Member
Subcommittee 109, Materials and Fabrication, Pressure Vessel and Piping Division
R. C. Dobbyn, Chairman
Subcommittee on Fatigue: PV and P. Div.
J. H. Smith, Chairman

American Welding Society
C. G. Interrante, H. I. McHenry and J. H. Smith, Members
Conference Program Advisory Board, Evaluation of Welded Structures Based on Fitness for Service
H. I. McHenry, Chairman
Technical Activities Committee
H. I. McHenry, Member-at-Large

Compressed Gas Association
Cylinder Specification Subcommittee
B. W. Christ, Member

Department of Energy
Subcommittee on Erosion/Corrosion of Turbine Materials
B. J. Hockey, Member

Department of Transportation
    Technical Pipeline Safety Standards Committee
        B. W. Christ and J. H. Smith, appointment by Secretary of Transportation

Electron Microscopy Society of America
    N. J. Tighe, Member

Interagency Coordination Group for the Application of Ceramics to Heat Engines
    S. M. Wiederhorn and N. J. Tighe, Members

International Commission on Glass
    Subcommittee VI A
        S. M. Wiederhorn, Chairman

International Institute of Welding
    Commission XV - Fundamentals of Design and Fabrication for Welding
        J. H. Smith, Member

International Powder Metallurgy Society (Planseeberichte für Pulvermetallurgie, Austria)
    J. G. Early, Member

International Society for Stereology
    R. deWit, Member

International Standards Organization (ISO)
    ISO/TC 164 on Mechanical Testing
        C. G. Interrante, Member
    ISO/TC 164/SC4 on Toughness Testing
        C. G. Interrante, Member
    ISO/TC 164/WG1 on Terms, Symbols, Definitions
        C. G. Interrante, Member

Maryland Institute of Metals
    R. deWit, Member

Mechanical Failures Prevention Group
    T. R. Shives and W. A. Willard, Editors

Metals Properties Council (MPC)
    Subcommittee 9 on Materials for the Gasification and Liquefaction of Coal
        J. H. Smith and R. C. Dobbyn, Members
    Technical Advisory Committee
        R. P. Reed

National Academy of Sciences (NAS)
    Project Advisory Committee on Investigation of Steels for Improved Weldability in Ship Construction
        H. I. McHenry, Chairman

Ship Materials, Fabrication and Inspection Advisory Group of the Ship Research Committee
H. I. McHenry, Member

National Institute of Ceramic Engineers
R. J. Fields, Member

National Materials Advisory Board (NMAB)
Committee on Reliability of Ceramics for Heat Engine Applications
S. M. Wiederhorn, Member

National Research Council
Committee on Recommendations for U.S. Army Basic Scientific Research
S. M. Wiederhorn, Member

New York Academy of Sciences
R. deWit, Member

Office of Energy-Related Inventions
J. G. Early, Reviewer of Invention Disclosures

Science and Technology, Office of the Assistant Secretary
Ad Hoc Committee for Technical Evaluation of a Proposal to Revive the Steelmaking Industry in Youngstown, Ohio
J. G. Early and J. H. Smith, Members

Sigma Xi
T. Chuang, J. G. Early, B. J. Hockey, R. S. Polvani and J. H. Smith, Members

Society for Natural Philosophy
R. deWit, Member

Standards Committee for Women
N. J. Tighe, Member

U.S. Civil Service Examiners for Metallurgist Interagency Board
J. G. Early, Chairman

Washington Academy of Sciences
R. deWit, Member and C. G. Interrante, Delegate on the Board of Managers

Washington Academy of Sciences Board of Managers
E. R. Fuller, Jr., Representative for Baltimore-Washington Chapter of American Ceramic Society

Washington Society for Electron Microscopy
B. J. Hockey and N. J. Tighe, Members

Welding Research Council (WRC)
- Long-Range Planning Committee
  - H. I. McHenry, Member
- Pressure Vessel Research Committee (PVRC)
  - C. G. Interrante and J. H. Smith, Members
- PVRC Hydrogen Embrittlement Subcommittee
  - C. G. Interrante, Member
- Subcommittee on Line Pipe Steels
  - M. B. Kasen and H. I. McHenry, Members
- Task Group on Field Welding
  - M. B. Kasen and H. I. McHenry, Members
- Weldability (Metallurgical) Committee
  - H. I. McHenry, Member

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B. W. Christ

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STANDARDS DIVISION

POLYMER SCIENCE AND STANDARDS DIVISION (563)

Ronald K. Eby, Chief
Leslie E. Smith, Deputy Chief
S. M. Thomas, Administrative Assistant
B. M. Weeks, Secretary

In the seven decades since Leo H. Baekeland introduced the first commercial synthetic plastic produced entirely by the reaction of small molecules, polymers have left little of our culture and technology untouched. We have moved rapidly into an age in which an overwhelming number of humanity's needs are served by polymers. The increase in production and use has been spectacular; the volume of polymers produced last year exceeded that of steel. Recent summaries show that polymers research already accounts for about forty-seven percent of the total industrial R&D expenditure for metals, polymers, and inorganic materials. Among these materials, polymers also constitute about thirty-nine percent of the value added by manufacture (a measure of the relative economic importance of manufacturing among industries), forty-five percent of the number of scientific publications, and thirty-nine percent of the ASTM standards.

Polymers have been shaped by intellectually sophisticated research which has been recognized by a number of Nobel Prizes. The resulting materials have contributed to national productivity through their economy, ease of fabrication, and useful properties such as low density, corrosion resistance, and toughness. They are energy efficient, with the largest volume polymer, polyethylene, using twenty-eight percent of the energy per unit volume required by steel for the conversion from raw to refined material and yielding further savings in processing and shipping.

Polymers have entered increasingly sophisticated and demanding applications. Polyvinylidene fluoride films are used as electromagnetic transducers in high fidelity systems. Structural parts of aircraft are composites with a polymer matrix. Polyurethane elastomers are used to pump blood in circulatory assist devices. The list of such examples is very long, encompassing trends for the increased use of polymers in packaging, construction, transportation, energy, electronics, information handling, clothing, appliances, dentistry, and medicine. Since polymer technology is on the steep part of the learning curve, these trends create new needs for concepts, measurements, standards, and data that can be used to insure reliable performance in use, processing, and other phases of the material cycle.

To identify the key needs, the managers of the Polymer Science and Standards Division make structured visits to Government and industrial laboratories. Recent visits have included Bell Labs, Du Pont, Army R&D Command, General Motors, Boeing, and Lawrence Livermore. Surveys have been conducted in the areas of durability, processing, and composites. These and other contacts with experts in industry, trade associations, standards associations, Government, and academia insure that the Division's efforts are directed toward fostering the effective use of polymers in solving national problems cited by our Director as appropriate for NBS. These include the growth of industrial productivity, prudent utilization of energy sources, a reasonable system for regulation of the effects of technology, and a wise policy of materials utilization.

The Division has used its survey activities as a basis for participating in budget initiatives to secure the resources necessary to meet the emerging needs. For the budget cycles currently active, programmatic initiatives that include additive migration, composites (biaxial orientation), blends, ionic conduction, and thin films are under consideration. Competence building initiatives on the science of collapse transitions, electronic conduction, high field NMR, and electron microscopy have been prepared.

The present activities are associated into areas concerned with mechanical reliability in load bearing applications, chemical durability, and lifetime prediction including the migration of protective additives, characterization methods and standards for molecular composition and use properties, dielectric properties, and electrical conduction, and reliable dental and medical materials. Substantial cooperative efforts are conducted with the Food and Drug Administration, the Department of Defense, the National Institutes of Health, the American Dental Association, the Department of Energy, the Bureau of Engraving and Printing, and others. All the efforts lead the scientists in the Division into productive examination of those properties of polymers which are of concern to people who use, design, and produce useful polymer objects. This work helps society capture, in safe and satisfying ways, the benefits of the increasingly widespread application of polymers.

The Division has had another productive year. It has fulfilled requests from other agencies and other NBS programs for $2.5 M worth of research services and has produced over seventy publications (about forty percent of the Center total). Seven members of the staff received outside recognition, and a similar number received Department of Commerce Awards. Three strong new staff members have been selected in the areas of charge conduction, chemical stability, and fracture. These include two highly qualified women professionals raising the Division's percent of minority and women full-time permanent professionals to twenty percent.

In the following pages, the activities of the Division are presented formally in five tasks, each described separately:

12132	POLYMER STANDARDS FOR CONTROL AND EQUITY
12135	TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS
12136	MECHANICAL DURABILITY OF POLYMERS FOR DESIGN AND USE
12138	MIGRATION AND THE DURABILITY OF POLYMERS
12139	DIELECTRIC AND PIEZOELECTRIC PLASTICS PERFORMANCE

POLYMER STANDARDS FOR CONTROL AND EQUITY
Task 12132

This task provides molecular and gas transmission standard reference materials (SRM's) to a $30 billion/year plastics and elastomers industry. Molecular SRM's are used extensively in industry to calibrate gel permeation chromatographs (GPC's) which are used routinely to measure polymer molecular weights and molecular weight distributions. The latter are the most important physical properties in determining a polymer's processability and its ultimate performance.

Our basic mission is to maintain and extend our expertise in polymer physical characterization. A fundamental knowledge of polymer solution properties such as osmotic pressure, viscosity, diffusional behavior, and scattering power is essential to this goal. As a consequence, a majority of the activities in this task involve experimental and theoretical studies of polymer solution properties. Some of these activities during the past year include:

- production of a new, narrow-fraction polystyrene standard, SRM 1479 ($M_w \sim 10^6$)
- completion of a new computerized gas permeation measuring facility
- continued development of a new state-of-the-art, self-calibrating GPC; self-calibration is achieved by making simultaneous light scattering measurements at nine angles on the GPC effluent
- characterization, by intrinsic viscosity and light scattering measurements, of a ultrahigh molecular weight polyethylene used in prosthetic devices
- development of the concept that all dilute polymer solutions possess certain "universal" physical properties characterizable by a single excluded volume parameter

Standards For Gas Transmission Rate Measurements
Subtask 1 of Task 12132

J. D. Barnes

Engineering work on the new NBS automated manometric permeation measuring facility is substantially complete. Operational trials and calibration measurements are currently under way. The efforts expended on the design of safety interlocks, control circuitry, interfaces, and operating software have provided valuable experience for future ventures in measurement automation. There are some improvements which must be made to the temperature controls and the vacuum manifold before routine experiments can be conducted.

Recent trends in gas transmission measurements have been toward instruments that are simpler to manipulate and more selective than the manometric technique. Our experience with our automated measuring system indicates that the manometric method is capable of considerable improvement at a relatively modest cost. The time scale of the measurements is determined completely by the diffusion coefficient of the gas, the thickness of the film being measured, and, in some instances, the time scale of concomitant viscoelastic processes. These factors are independent of the technique used to measure the transport properties. The optimization that is built into the controlling software we have devised does, however, result in significant time savings because there is no need for a human decision regarding the recovery of the system from the previous measurement cycle or the achievement of a steady state. The experience should prove useful to those who wish to devise simpler instruments for use in quality control applications.

The new facility was used to investigate the feasibility of adding transmission rates for He, N_2, and CO_2 to the certificate for gas transmission SRM 1470, which is currently certified only for oxygen. These preliminary experiments demonstrated that the apparatus obtains valid data for these gases. An experimental design has been formulated for carrying out the measurements of transmission rates of He, N_2, O_2, and CO_2 at a number of pressures and temperatures as required for an SRM certificate. OSRM is providing support for these measurements, and it is expected that they will be complete by the third quarter of FY81. The measurements of O_2 permeance are being redone because it is expected that some aging of the material has taken place during storage.

Correlations which are possible when four different gases with different molecular sizes and different thermodynamic properties are measured on the same sample should provide a clearer picture of the gas transport mechanisms in this polymer.

The preliminary experiments revealed, as expected, that CO_2 exhibits the phenomenon of partial immobilization in SRM 1470. New models must be devised for fitting the experimental data, and the ramifications of partial immobilization on the mechanical properties and morphology of the polymer must be explored before we can specify the best way to use SRM 1470 in calibrating CO_2 permeance measuring apparatus.

A publication describing the construction and operation of the automated manometric permeation measuring apparatus will be prepared as time becomes available once the apparatus is being used for routine measurements.

After completing the recertification of SRM 1470, we expect to evaluate candidate materials for an SRM with transmission rates approximately 50-100 times that of SRM 1470. These materials are needed because existing instrumental methods perform poorly at high gas fluxes. It is likely that minor changes will have to be made in our interfaces in order to accomodate the higher data collection rates found in this work.

Work is continuing on devising a system of units that is both compatible with SI and scientifically consistent. The SI base units of moles, meters, pascals, and seconds are the starting point. While the logic of this scheme is recognized, there is considerable resistance from users of the wide variety of customary unit systems.

A publication outlining ways in which SRM 1470 can be used to improve the performance of existing gas transport measurement systems is in preparation.

NBS played an influential role in promulgating a substantially revised edition of ASTM D-1434, the standard method for measuring gas transmission rates. The new document features more consistent terminology, an improved set of SI units, the use of safer equipment, the use of SRM 1470 for calibration checking, and a clearer derivation of the equations used to fit the data.

ASTM Activities
Subtask 2 of Task 12132

J. D. Barnes

J. D. Barnes serves as Chairman of ASTM Subcommittees F-2.30 (Test Methods) and F-2.93 (Statistical Matters) of ASTM committee F-2 on Flexible Barrier Materials. Subcommittee F-2.30 is currently working on test methods relating to materials characterization, barrier properties, sealing and bonding properties, and additive migration. Subcommittee F-2.93 is responsible for providing statistical assistance to all task groups operating within F-2. The design and analysis of interlaboratory testing programs are the major forms this assistance takes.

Dr. Barnes and Dr. John Mandel conducted a workshop on Interlaboratory Testing during the February 1980 ASTM Committee Week in San Diego, California. Over 100 individuals from ASTM Committees D-20, F-2, and F-17 participated. Interlaboratory testing programs are the principal technique used to validate ASTM Methods of Test.

Dr. Barnes is also a member of ASTM Committee D-20 (Plastics) and its subcommittees on Plastic Film and Sheeting D-20.19, Olefin D-20, and F-2. Dr. Barnes led the task group that recently promulgated a revised version of ASTM D-1434, the standard Method of Test for Gas Transmission Properties of Plastic Film and Sheeting.

Self-Calibrating Gel Permeation Chromatography
Subtask 3 of Task 12132

P. H. Verdier

Gel permeation chromatography (GPC) is a widely accepted technique for estimating the molecular weight distribution (MWD) of high polymers. However, the usefulness of the conventional GPC apparatus is limited by the need to provide calibrants for each polymer measured of known molecular weight over the entire molecular-weight range in which the MWD is significantly different from zero. The calibration depends, among other things, upon the chemical nature, degree of branching, etc., of the polymeric material, so that each new material requires a fresh calibration. The so-called "universal calibration" hypothesis, while useful, is limited to comparisons of polymers of similar shape, and in any event, is inadequate for quantitative determinations. Some instruments, an example of which is commercially available, attempt to circumvent the need for calibrants by adding a single-angle light scattering detector to the usual concentration-sensitive detector. However, this does not allow the extrapolation to zero scattering angle which is required in principle to relate scattering intensity to molecular weight. In addition, qualitative information on the variation of scattering with angle, normally required to give assurance that meaningful results are being obtained, is not available.

We are designing and constructing a light-scattering detector for the GPC which measures, in real time, the scattering intensity as a function of scattering angle, and which is controlled by a dedicated minicomputer in a way that allows scattering to be measured as a function of scattering angle and concentration. The instrument will allow continuous monitoring of the variation of scattering with angle. This will allow immediate identification of difficulties such as association, microgel formation, etc., which could affect the validity of the molecular weight obtained, an important consideration for work on new and unstudied materials. In addition to molecular weight, the mean-square radius (radius of gyration) will be obtained as a function of molecular weight, at least in the higher ranges of molecular weight, providing useful information for the characterization of branched polymers.

The instrument has been designed, and construction of its mechanical components is scheduled for completion by the end of the current fiscal year. The dedicated minicomputer system has been installed, with a video display which will permit real-time plotting of the angular dependence of the scattering. In the coming fiscal year we expect to assemble and align the instrument and begin testing.

Dynamics of Polymer Chains
Subtask 4 of Task 12132

P. H. Verdier, D. E. Kranbuehl

The dynamic behavior of polymer chains is important for two reasons. First, the principal methods used to estimate molecular weight, and in particular gel permeation chromatography, the only method available at present for estimating distribution in molecular weight, are dynamical, non-equilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. In its present state, the theory of these systems does not allow the calculation of molecular weight directly from measured quantities; a series of calibrants of known molecular weight is required. Improvements in the theory could reduce or even remove the need for calibrants, allowing the determination of molecular weight distribution of polymers for which calibrants are not available.

Second, the processability and the final characteristics of both plastics and elastomers depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. More realistic theoretical treatments of polymer melts and elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, will lead to more efficient processing and better fabricated end-products. A major shortcoming of the present theory is its inability to treat chain entanglements in a realistic way. Our present work is aimed primarily at the study of entanglement effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on simple model systems and serve to guide the development of better theoretical treatments.

We have previously shown that for our simple chain models, self-entanglement effects lengthen the longest relaxation times of the chains by a factor proportional to about the first power of chain length. However, our models differ from polymer chains in solution in (at least) two obvious respects: the chains are constrained to lie upon a lattice, and motion from one configuration to another is accomplished solely by a series of purely local chain motions. Theoretical work carried out elsewhere appeared to predict a much weaker dependence of the lengthening of relaxation times upon chain length than we had found, leading to the suggestion that our results were artifacts arising from special constraints in the local chain motions we had employed. We subsequently obtained results for chains with modified rules of motion free of these constraints and showed that the suggestion was incorrect. We have now completed a series of studies of the effects of local bead motion constraints and of the type of lattice employed upon relaxation behavior. The results show that although self-entanglement effects are weakened by the removal of local bead motion constraints, they are still much stronger than current theoretical predictions. Further, the self-entanglement effects are essentially the same on simple cubic, body-centered cubic, and face-centered cubic lattices, suggesting that similar behavior may be obtained when the chains are removed from the lattice. Therefore, we are preparing to study the motion of chains free of lattice constraints (though still employing local bead motions). Testing of the programs is currently under way. We expect that it will be completed and preliminary results obtained by the end of the current fiscal year; the study should be completed in the coming fiscal year.

Additional work planned for the coming year will proceed along two lines. First, there is at present an unresolved disagreement in the literature regarding the interpretation of the time-correlation functions obtained for flexible chain molecules in the quasielastic light scattering experiment. It is not clear whether these functions exhibit the entire spectrum of chain relaxation times or are dominated by the longest relaxation time. It appears that by direct simulation we may be able to resolve the disagreement, which will increase the value of measurements made by this relatively new technique. Second, as a step in the direction of investigating melt properties, we will extend the simulation studies to non-dilute solutions.

Static and Dynamic Scattering From Polymers
Subtask 5 of Task 12132

C. C. Han

Scattering techniques are most effective in measuring space as well as space-and-time correlations of polymers in both solutions and bulk states. Our effort has been centered around the universal approach of temperature, molecular weight, and concentration dependence of static and dynamic properties of polymers. We investigate and compare theoretical predictions based on modern scaling concepts as well as conventional theories to our experimental results from the small angle neutron scattering (SANS), light scattering, and quasielastic light scattering experiments.

In static scattering, spatial correlations of monomer densities in q-Fourier space are measured directly. With the SANS facility at NBS, it is possible to measure single chain properties in the range of $0.01 \leq q \leq 0.1\ \text{Å}^{-1}$ from dilute solution to the bulk state through deuterium labeling. Also, with the high concentration labeling technique which we developed last year, it is possible to study single chain properties over a wide range of concentrations using a medium flux reactor such as the NBS reactor.

On the other hand, dynamic scattering, such as quasielastic light scattering, uses the photon correlation technique to measure the time correlation function of scattered light from polymer solutions. This time correlation function at any momentum transfer, q, is related to the intermediate scattering function, S(q,t), which is a Fourier transform of the space correlation function of monomer pairs. Therefore, in principle, measurement of S(q,t) can provide not only a measure of the properties associated with the equilibrium distribution of polymer segments such as the radius of gyration, R_G, or the statistical segment length, but can also measure physical properties associated with the time evolution of polymer segment distributions, such as the hydrodynamic radius, R_H, or the hydrodynamic interaction strength.

Our most recent efforts have been centered on the development of theories for the intermediate scattering function, S(q,t), and the characteristic frequency, $\Omega(q)$, for polymer solutions. Such theories are essential for the interpretation of quasielastic light and neutron scattering data. Our theory includes both temperature and molecular weight dependence specifically. We have also successfully applied this theory to a different characterization technique, intrinsic viscosity.

Interpretation of Scattering Experiments on Polymer Solutions
Subtask 6 of Task 12132

A. Z. Akcasu[1], M. Benmouna[1], C. C. Han

[1]University of Michigan

Interpretation of dynamic scattering experiments requires, ideally, a theory that can predict the intermediate scattering function, S(q,t), and a chain model consistent with the chemical structure of the polymer. Unfortunately, exact expressions of S(q,t) are available, at present, only for single unperturbed (θ-condition) gaussian chains without hydrodynamic interaction (Rouse model), or, in the infinite chain limit, with hydrodynamic interaction and preaveraged Oseen tensor (Rouse-Zimm model). In this sense, a complete interpretation of scattering experiments on polymer solutions is an unsolved problem. By using linear response theory, we have been able to obtain closed form expressions for S(q,t) of both linear and circular chains for Rouse and Rouse-Zimm cases in the infinite chain limit. Also, we can express S(q,t) for finite linear chains in the Rouse limit and for circular chains in both Rouse and Rouse-Zimm limits in closed form. All these can be compared with the method of eigenfunction expansion and the method of solving diffusion equations directly. Advantages of our current scheme have been demonstrated. In the case where an exact solution of S(q,t) can not be obtained, the characteristic frequency, Ω(q), which is the initial slope, and defined by

$$\Omega(q) = -\lim_{t \to 0} \frac{dS(q,t)}{dt}$$

can be calculated. The temperature and concentration dependence of Ω(q) in terms of "blob model" chain statistics can be calculated not only for the intermediate scaling region, but also for the upper and lower transition regions where information about polymer chain parameters such as radius of gyration, R_G, statistical length, a, and hydrodynamic interaction, B, can be extracted.

Temperature, Molecular Weight, and Concentration Dependence of Chain Dimensions Around θ-Temperature
Subtask 7 of Task 12132

S. J. Bai[1], D. J. Lohse[2], I. C. Sanchez, C. C. Han

[1]IAP assignment from University of Michigan
[2]NRC/NAS Postdoctoral Associate

Chain dimension and the q-dependence of the single chain scattering function, S(q), are being studied at various temperatures and concentrations with different molecular weights by SANS. Experimental results will be compared with various theroetical predictions. The difference between dimensions in dilute solution at the θ-temperature and in the bulk state will be studied.

Concentration Dependence of Diffusion Coefficient at Various Molecular Weights and Temperatures
Subtask 8 of Task 12132

A. Z. Akcasu[1], C. C. Han

[1]University of Michigan

Experimental results of the concentration coefficient, k_D, of the diffusion coefficient, D, of polymers in dilute solution have been investigated and compared with various theoretical predictions. The negative k_D for small molecular weight and low temperature and the positive k_D for large molecular weight and high temperature can be understood through model calculations which include chain swelling and intermolecular potential. The molecular weight independent, but negative, concentration dependence of D at θ-temperature indicates the contributions of overlapping pairs of molecules. Chain expansion at the θ-temperature due to chain overlap is implied.

Dynamic Structure Factor, S(q,ω), of Dilute Polymer Solutions
Subtask 9 of Task 12132

A. Z. Akcasu[1], C. C. Han

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Most of the quasielastic neutron and some of the quasielastic light scattering experiments are performed in the frequency domain due to the characteristics and availability of experimental facilities. The extraction of the characteristic frequency Ω(q) from S(q,ω) data poses difficulties similar to those in time domain analysis. Although S(q,ω) is just the Fourier transform of S(q,t), it is not straightforward to obtain an analytical expression for S(q,ω) even in the cases where S(q,t) is available. On the other hand, it is not fruitful to perform numerical inverse Fourier transform on the experimental S(q,ω), due to the finite data set and lack of precision. We have, therefore, investigated the shape of S(q,ω) numerically for various cases to facilitate the extraction of Ω(q) from S(q,ω) directly in both light scattering and neutron scattering experiments.

Domain Structure of Block Copolymers and Characterization of Polyelectrolyte
Subtask 10 of Task 12132

I. Noda[1], T. Hashimoto[2], S. J. Bai[3], D. B. Minor, and C. C. Han

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[3]IAP assignment from University of Michigan

Preliminary study of the domain interface structure of star shaped polystyrene-polyisoprene block copolymers has been carried out by neutron scattering. Data analysis is in process, and further experiments are in preparation.

Also, the characterization of polyacrylic acid by combined measurement of SANS and LS under various salt concentrations and charge densities is under way.

Development of a Digital Lock-in Light Scattering Photometer, and the Measurement of Polystyrene 1479 and UHMW Polyethylene
Subtask 11 of Task 12132

D. B. Minor, H. L. Wagner, C. C. Han

A state-of-the-art light scattering photometer has been developed for the purpose of measuring the molecular weight of polymer SRM's and ultra high molecular weight synthetic implant materials. This photometer, which utilizes photon counting and digital lock in, has been tested by measuring previously certified SRM's.

A temperature controller has been installed and tested for polyethylene measurements at elevated temperatures. Measurement of polystyrene 1479 ($M_w \sim 10^6$) in toluene has been completed for SRM certification. Measurements of ultra high molecular weight polyethylene is currently under way.

Configurations of Polymer Chains
Subtask 12 of Task 12132

R. J. Rubin

A review of applications of the theory of random walks to polymer chain configurations is being prepared with G. H. Weiss of the National Institutes of Health. This review also includes a number of new results: (1) a new connection has been established between random walk probability distributions and a generating function obtained by Rubin [J. Chem. Phys., 43, 2392 (1965)] for calculating configurational properties of a polymer chain attached to an adsorbing (or repelling) solution surface. In particular, eq. (26) of that paper can be expanded as a power series in e^{θ}. The coefficient of $e^{s\theta}$ is the probability that a random walk originating in the solution surface layer will return s-1 times to the surface in an N-step walk. Random walk probability distributions of this type are considered by E. W. Montroll and G. H. Weiss, [J. Math. Phys., 6, 167 (1965)]. When Rubin's eq. (26) is viewed in this way, random walk configurations are classified according to the number of visits, s, to the surface layer. Then the total probability is the sum of the weighted probabilities where the weight function is proportional to $e^{s\theta}$, a Boltzmann weight factor. (2) The treatment of a polymer chain between two plane solution surfaces given by DiMarzio and Rubin [J. Chem. Phys., 55, 4318 (1971)] has been extended to treat polymer chains of finite length. All the results obtained by DiMarzio and Rubin pertain to the limit in which the ratio of the extended chain length to the separation between the bounding planes is large compared to unity. One quantity of particular interest is the average step density as a function of position between the solution surfaces. For random walks of N steps, configurations can be classified according to the number of visits, r,s, to the two solution surfaces. The subclass of N-step random walks in which each surface is visited at least once is identical to the subclass of N-step random walks whose span is the same as the distance between the solution surfaces. The calculation of the step density for N-step random walks with a given span is in progress.

In the absence of the complicating effects of interaction with surfaces, probability distribution functions of configurations of long chain molecules can be modeled by solutions of a random flight or diffusion equation. However, it is known from studies of lattice models that if the energy of attraction between links of the polymer chain and the surface becomes sufficiently high, then there is a discontinuous collapse of the chain on the surface. The description of such discontinuous behavior within the framework of a diffusion equation appears to present technical difficulties.

DeGennes [Reports Prog. in Phys., 32, 187 (1969)] has proposed that the appropriate boundary condition in the case of a "weakly adsorbed" chain is the mixed boundary condition, $\ell \, \partial G/\partial x + mG = 0$ at the solution surface, where $G(x,N)$ is the solution of the diffusion equation. DeGennes drew the analogy between his suggestion for the boundary condition of the diffusion equation and the treatment of the bound state of the deuteron. We have approached the question of the appropriate boundary condition for the diffusion equation in a complementary way. Starting with the lattice random walk equations in Rubin [J. Chem. Phys., 43, 2392 (1965)], we have assumed that not only the surface layer is modified by a factor e^{θ}, but each of the first ℓ layers are modified by this factor. We then go to the random flight limit in which the lattice equations are replaced by diffusion equations.

For this special model, we see how to establish a correspondence between the solution of a diffusion equation with a source (sink) term in an adsorbing (repelling) layer with an absorbing boundary condition and the solution of a diffusion equation with the mixed boundary condition proposed by DeGennes.

The Characterization of Ultra-High Molecular Weight Polyethylene For Synthetic Implants
Subtask 13 of Task 12132

H. L. Wagner, J. G. Dillon[1]

[1]Guest worker, Food and Drug Administration

The development of new or modified methods for characterizing the molecular weight and molecular weight distribution of ultra high molecular weight polyethylene (UHMWPE) has continued with major emphasis on work on the low shear viscometer. The light scattering apparatus has been readied for high temperature operation, and a new fractionation bath is being assembled.

Because of problems with wobble of the rotor and poor reproducibility, major modifications were made in the viscometer design. As a result of these changes, it is now possible to reproduce solvent readings to within one percent, and the wobble of the rotor is no longer noticeable at those periods of rotation required for viscosity number determinations.

A problem remains with reproducibility for solutions of UHMWPE which appears to be due primarily to solution preparation. If severe enough means are not employed to dissolve the polymer, complete solution is not obtained. If too severe a method is used, on the other hand, degradation occurs. Considerable effort has gone into finding a satisfactory technique, and a promising one is now being evaluated. It consists of heating the solution at 150 °C under nitrogen for one hour with just enough gentle swirling to keep the polyethylene particles separated before melting. This avoids the formation of globs which are very difficult to dissolve.

Viscosity values in decalin in the low shear viscometer are some twenty percent higher than in tetralin, a surprising result, since if the Mark-Houwink equations (evaluated for lower molecular weights) are extrapolated to higher molecular weights, very similar viscosity numbers would be expected for these solvents. It is also found that these high values in decalin decrease at the rate of two to three percent per hour for the first few hours, a change which does not occur with tetralin or with either solvent in the ordinary capillary viscometer, which operates at much higher shear rates. Whether these differences are due to degradation or some other phenomenon has not been determined.

Once the technique for obtaining low shear viscosity numbers is established, fractionation will begin in order to obtain fractions for establishing the Mark-Houwink equation for UHMWPE.

Cell Model Theory of Polymer Solutions
Subtask 14 of Task 12132

I. C. Sanchez, D. J. Lohse[1]

[1]NRC/NAS Postdoctoral Associate

An incompressible, statistical thermodynamic theory of a polymer solution is formulated which takes into account concentration inhomogeneities. A generalized cell model is used as the basis for the new polymer solution theory. Closed-form, parametric equations are obtained for solvent and polymer chemical potentials which only reduce to classical (Flory-Huggins) potentials when concentration homogeneity is assumed. In a good solvent, the calculated second virial coefficient decreases with molecular weight ($M^{-1/5}$ dependence) in good agreement with available experimental data. In dilute solutions, chain dimensions can be analytically determined; the well-known Flory excluded volume equation is obtained. The most important parameter in the cell model is the average number of chains/cell, λ. For semi-dilute solutions ($\lambda >> 1$), it is shown that several important scaling results are recovered from a simple scaling hypothesis for λ.

Interfacial Tension Theory of Low and High Molecular Weight Liquid Mixtures
Subtask 15 of Task 12132

I. C. Sanchez, C. I. Poser[1]

[1]Guest Worker, University of Massachusetts

A generalized van der Waals or density gradient theory of interfaces has been combined with a compressible lattice theory of homogeneous fluid mixtures. Binary liquid-vapor and liquid-liquid systems are treated. For non-polar low molecular weight mixtures, liquid-vapor tensions are calculated as a function of composition with an error of less than five percent. These calculations involve no adjustable parameters; all required parameters are determined from pure component properties. For polymer solutions, it is usually necessary to introduce an adjustable interaction parameter to accurately correlate liquid-vapor tensions. Approximate equations for the interfacial tension and thickness between two immiscible, high molecular weight polymer liquids have been obtained. These equations are a function of a single interaction parameter; when this parameter is chosen to match experimental tensions, interfacial thicknesses of 1 to 5 nm are obtained. To assess the importance of compressibility effects, the interaction parameter can be chosen so that the heat of mixing is zero for an incompressible system. This "pure compressibility approximation" works well for polymer pairs with relatively low interfacial tensions. The most serious deficiency of the theory is that intramolecular correlational effects present in long polymer chains are only crudely approximated.

Configurational Properties of Comb-Branched Polymers
Subtask 16 of Task 12132

F. L. McCrackin, J. Mazur

Mean-square radii of gyration were computed for comb-branched polymers simulated on a cubic lattice by chains with both excluded volume and attractive energies between nonbonded segments of the polymer. The ratios, g, of the radius of gyration of a comb-branched polymer to that of a linear polymer of the same molecular weight at the theta point were found to be larger than the g ratios calculated by the unrestricted random-walk model of the polymer. These calculated g ratios showed better agreement with experimental measurements than did those calculated by the random walk model.

The radii of gyration of the backbones and the expansion factors of the comb-branched polymers were also calculated. The radii of gyration of the backbones at the theta condition were greater than that of linear polymers, in contradiction to the random walk model which requires that they be equal. The calculated expansion factors were less than that of linear polymers, also in contradiction to the random walk model.

Rubber and Rubber Compounding Standard Reference Materials
Subtask 17 of Task 12132

G. W. Bullman, G. B. McKenna

The process of streamlining the NBS Rubber Program is continuing in response to reduced resources available for this program. As part of this reduction, rubber and rubber compounding Standard Reference Materials, for which NBS serves primarily as a warehouse facility, are being removed from the SRM list as inventories are exhausted. In addition, several materials are being removed from the list due to poor sales. These SRM deletions are being coordinated with ASTM Committee D-11 on Rubber and Rubber-like Materials and Committee D-24 on Carbon Black to assure an orderly change in the ASTM standards and within the rubber industry.

In order to serve industry's needs for rubber SRM's with our reduced resource base, we are maintaining inventories of materials which industry (through ASTM) has indicated are important, even though NBS's primary function for these materials is to serve as a warehousing facility. For example, we are recertifying N-tertiary-butyl-2-benzothiazole sulfenamide [SRM 381(d), a rubber accelerator] in order to maintain inventories of this material. In addition, where standards involve certification of basic physical properties, we are assuring the renewal of the SRM's as necessary, and where the need is indicated, we are issuing new SRM's. Thus, last year we recertified the butyl rubber SRM 388(k) which is used as a Mooney Viscosity Standard. During this year, we have completed the work necessary for procurement of a new Mooney Viscosity Standard, thus extending the range of Mooney Viscosity Standards available to the rubber industry.

TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS
Task 12135

The objective of this research is to contribute to dental health care through development of better performing materials and test methodology and standards appropriate thereto. Materials research and techniques are pursued with the goal of developing adhesive composite restorative materials of greater durability and wear resistance, and improved base metal alloy alternatives to the costly gold alloy prostheses. Knowledge of the structure and physical chemistry of biologically important calcium phosphates is used to develop improved preventive dental techniques. Improved test methodology is sought for characterization of the surfaces of surgical implant materials and for defining the interactions that occur thereon.

Dental research directions in support of the objective are established collaboratively with the American Dental Association, the National Institute of Dental Research, and the Department of Defense R&D command. Medical materials research is guided by close interaction with the Food and Drug Administration's Bureau of Medical Devices and the ASTM F-4 Committee (Medical and Surgical Materials and Devices).

Dental Composite, Resin, Sealant, and Cement Chemistry and Development
Subtask 1 of Task 12135

G. M. Brauer, J. M. Antonucci, J. W. Stansbury, R. E. Dehl, J. M. Cassel, R. L. Bowen[1], H. Argentar[1], D. W. Misra[1], T. Chen[2]

[1]Research Associate, American Dental Association
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Current efforts are directed toward upgrading the quality of composite restorative materials with regard to color and storage stability, toxicity effects, adhesiveness, and durability. Structure-property relationships are developed and used as guides to the synthesis of new polymerization accelerators for dental resins. Laboratory synthesis and evaluation efforts have developed an amine accelerator with a reactivity that permits a threefold reduction in the concentration of accelerator required. The generic biocompatible nature of the amine, combined with the reduced concentration required, indicates that dimethylaminophenylacetic acid will prove a valuable dental resin component. Strong interest has been expressed by the dental manufacturers in a second amine developed to accelerate the curing of denture base materials without imparting any color. Efforts have continued to make a potentially very useful peroxide ascorbic acid copper initiator accelerator system more practicable. Invited papers covering initiator accelerator systems for acrylic resins and composites and new monomers for use in dentistry were presented at the Symposium on Biomedical and Dental Applications sponsored by the ACS in Houston.

The mechanism of reinforcement of dental composite restorative materials through silane inorganic fillers is being examined as a means of improving the durability of such materials when used in stress bearing applications. Bond formation between the silane coupling agent and the filler is monitored by infrared analysis and indicates that addition of selected amines to the carrier solvent improves the coupling effectiveness of the silane.

A major problem encountered in the investigation of the properties of dental composite restorative materials is the absence of quantitative analytical methods for determining chemical composition in the solid state. Infrared (IR) spectroscopy, which is widely used to analyze chemical composition, is useful for studying dental composites, but Fourier Transform capability is required because of light scattering and absorption by the glass filler. Measurements are currently being made with the new IR equipment of the Center for Materials Science. Recently we have performed some Raman spectroscopic analyses of dental composites and the various components of the composites, using the spectrometer in the Center. Preliminary results indicate that the Raman technique will circumvent many of the problems encountered with infrared analysis and will allow at least semiquantitative estimates to be made of chemical groups such as unreacted carbon/carbon double bonds in the polymerized composite matrix. Further work is in progress, as we use the Raman technique to analyze dental composite materials prepared by different experimental procedures. We are also investigating NMR as a means of studying the state of molecular motion in these presumably highly cross-linked resin systems. It is expected that the information thus obtained will be useful in evaluating the performance of dental materials.

At the request of the Council on Dental Materials, Instruments, and Equipment of the American Dental Association, a status report for publication in the Association's Journal was prepared on the desirability of using radiopaque plastics in dentistry.

Development of Adhesive Bonding Technique
Subtask 2 of Task 12135

G. M. Brauer, R. L. Bowen[1], J. M. Antonucci, D. W. Misra[1],
J. W. Stansbury, J. M. Cassel

[1]Research Associate, American Dental Association

Strong mechanical bonding of acrylic resins to enamel surfaces can be obtained through acid etching of such surfaces, followed by resins or composite formulations capable of wetting and penetrating the newly created surfaces. Such treatment has not been applicable to surfaces of dentin and has not been entirely successful in the caries preventive application of pit and fissure sealants to the occlusal enamel surfaces of children's teeth.

One approach to adhesive bonding that is being pursued is the development of multifunctional molecules designed to interact with calcium on the tooth surface and with the *in situ* polymerizing dental resin. Using the diametral tensile strength of hydroxyapatite filled composites as a measure of the adhesiveness where the filler is coated with the coupling agent of interest, several surface active polymerization activators appear to offer promise.

One new direction taken recently has been the development of physiological buffer solutions capable of dissolving the smeared surface layers on cut dentin and of isotonic mordant solutions to improve bonding sites. Isotonic methacrylate monomer formulations containing adhesion promoting coupling agents have been developed that should not induce osmotic insult to odontoblasts and pulp tissues.

Wear Resistance and Mechanical Properties of Dental Materials
Subtask 3 of Task 12135

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[1]Guest worker, Georgetown University Dental School

In a study of the mechanisms governing both clinical and laboratory wear of dental restorative materials, a silver staining technique has been developed to examine structural changes in the damage zone immediately beneath the worn surface. Worn specimens are cross sectioned and examined by microscopy for quantification of the micro defects. Initially, clinically worn specimens are being provided through a guest worker from Georgetown University Dental School. The results to date suggest that greater efforts to introduce erosion effects into accelerated wear testing are required. Equipment to accomplish this has been designed and assembled.

With pin-on-disc wear instrumentation we have demonstrated that wear is very irregular, varying by a factor of two over different positions on the same specimen. The data support the use of durapatite, a form of sintered hydroxyapatite, as an appropriate substitute for human tooth enamel for in vitro measurements. However, microdefect analysis of in vivo and in vitro worn specimens brings into question the relevancy of in vitro data generated with enamel pins. The effect of loading on the accelerated wear results generated on dental composite specimens with hard (durapatite) and softer (steel) pins is under study. Initial transient wear regions indicate the presence of surface layers that inhibit wear of certain metals and alloys. These surface layers reform during periods of inactivity. Since this phenomenon may play a very important role in enhancing in vivo durability of amalgams and other dental alloys, efforts are in progress to determine surface compositions by means of Auger Electron Spectroscopy.

Auger Electron Spectroscopy (AES) Applied to Wear Analysis of Dental Alloys
Subtask 4 of Task 12135

J. M. McKinney, R. E. Dehl, W. H. Grant

In vitro accelerated wear measurements on several dental alloys have been characterized by low initial wear rates followed by higner steady state rates of wear. We have attributed this behavior to the formation of a passive oxide surface layer, with higher wear resistance than the bulk material, that is reformed during periods of mechanical inactivity.

We have initiated examination of these surface layers by AES. Following a period to develop familiarity with the instrumentation (Surface Science Division, Center for Thermodynamics and Molecular Science) and confidence in the technique, measurements have been made on an amalgam, on three crown and bridge alloys, and on nickel as a standard. Preliminary measurements by argon ion sputtering of the surfaces to a depth of 10 nm has indicated distinct changes in composition as a function of depth into the surface layer. It is planned to generate AES depth profiles on a number of dental alloys with a goal of correlating surface layer analysis to the *in vitro* wear and finally to *in vivo* durability. Analysis of wearing surface layers may prove important for long-term biocompatibility consideration including toxicity, chemical irritation, sensitization, and gingival inflammation from plaque.

Porcelain Fused to Base Metal Alloys
Subtask 5 of Task 12135

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This investigation is designed to develop knowledge of the physical, mechanical, and chemical properties of porcelain veneering alloys and their associated bonding porcelains relative to their use in cast crown and fixed partial dentures; to determine the effects of fabrication techniques on clinical serviceability of the restoration; to investigate factors affecting the bonding of porcelain to new dental alloys; and to determine potential methods for modification of fabrication techniques which may lead to improved clinical service. The chemical, physical, and mechanical properties of new, non-precious alloys are so different from those of the gold alloys that the application of the same fabrication techniques for porcelain bonding could be expected to be unsuccessful. This has proven to be the case, and not enough is yet known to render non-precious metal porcelain restorations as trouble free as gold porcelain restorations.

It is suspected that a major cause of porcelain metal failure resides in the residual stress which develops upon cooling of fired porcelain restorations. To address this problem, a multi tiered approach has been taken: (a) development of precise knowledge of the thermal expansion behavior and other mechanical and physical properties of porcelain and alloys after being subjected to dental laboratory firing conditions; (b) the fabrication, according to dental laboratory fabrication procedures, of split ring composites of porcelain (opaque plus body) veneered to alloys and determination of the accompanying change in gap; (c) the development of finite element model and elasticity analysis to examine the residual stress states and accompanying gap changes; and

(d) examination of porcelain and alloy for microstructural characteristics as well as examination of the microstructure of the porcelain alloy composite for stress induced (or other) flaws. Ultimately, the data developed in (a) and (b) will be used in the theoretical program in (c) to determine the "macroscopic" residual stress states developed in the split ring. The analyses may further be developed with the knowledge developed in d), which may involve the superposition of microscopic stresses on the macroscopic stresses.

Results obtained thus far have shown that significant differences exist in expansion of porcelains which have received comparable levels of firing according to manufacturers' instructions. Differences exist between manufacturers' porcelains, and some develop significantly different expansions with repeated firing. Large differences in the amount of residual stress are fired into different porcelains, as indicated by the amount of stress relief which occurs.

As compatibility depends not only on the stresses set up by differences in thermal contraction, but on geometrical shape and the thermal (or other) relief of stress, a split ring was conceived as presenting a reasonably close approximation to a clinical crown while providing a technique to assess the development of residual stress. Experimental and theoretical results of studies of gap and shape changes indicate that a previously derived mathematical expression is not sufficient to describe the complex interactions which exist and that discrepancies between theoretical and experimental results indicate stress relief at temperatures lower than T_g. These effects will be evaluated with refinements to finite element model and in view of the differences in crystallinity which have been shown to exist by Raman laser spectroscopic observations of the porcelains.

<u>Dental Casting Alloys</u>
Subtask 6 of Task 12135

J. A. Tesk, R. M. Waterstrat[1], R. W. Hinman[2], E. E. Parry[2]

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The commercial alloys now available for dental castings contain significant amounts of gold, silver, palladium, cobalt, nickel, and chromium. These metals formerly were abundantly available, but in recent years there have been sharp fluctuations in the price of these materials. It appears that the market for these metals will continue to be increasingly unstable, since there are no viable domestic sources of the ores, and the United States must import these metals from foreign countries which are susceptible to political or economic upheavals. The cost of these alloys is an important factor in dentistry; and in order to avoid future problems, it is prudent to plan some strategies to meet unexpected shortages or sharp increases in price. This can be accomplished by developing alternate alloys, and particularly those whose ores are available domestically. Titanium is an example of one such alternate.

We have demonstrated that it is possible to produce precision dental castings based on titanium, but it is necessary to define the basic properties of these alloys before any laboratory castings can be produced for clinical use. During the past year, biocompatibility studies were completed on a titanium-13 percent copper alloy in cooperation with Dr. Frank Young at the Medical College of South Carolina. The results indicate that the alloy is very well tolerated in soft tissues. This is an important step toward eventual clinical trials in humans.

The ease with which a molten alloy fills the refractory mold cavity during the casting process is another problem that has been associated with the use of non-precious alloys. In an effort to ascertain the magnitude of this problem, an objective procedure for measuring the "castability" of dental alloys was developed as an early phase of this project and identified in a previous report. Early data resulting from this test method were plagued by unacceptably high variability. More recently, a modification of the pattern sprue has been tested, which results in much improved data. Using this procedural modification, extensive study has been undertaken to illustrate the differences in castability for various alloys when following the manufacturer's casting instructions. This work suggests that some non-precious alloys are relatively easy to manage in the laboratory. Early subjective clinical laboratory results appear to correlate quite well with measured values gathered in this project. The development of an objective technique to assess the correlation with margins on clinical crowns is desirable and will be pursued.

<u>Dental Ceramics</u>
Subtask 7 of Task 12135

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[1]Research Associate, American Dental Association

Work continues on the formulation of lower fusing dental porcelain frits prepared by the gel route. Frits have been made by the gel route which mature in a 12 minute air fire at 822 °C. These appear suitable for metal ceramic applications and have a thermal expansion greater than 12×10^{-6}/°C between 23 and 400 °C. A high expansion rate is desirable to match those of some metals. The fusion or maturation temperature is 125 °C lower than the current lowest fusing commercial metal ceramic porcelain. Solubility of the low fusing porcelain is in the range of current commercial products. Deformation temperature under applied load is about 650 °C, the same as many other metal ceramic body porcelains.

Other porcelain frits have been formulated which fuse at lower than 900 °C. Some of these have thermal expansions greater than 14×10^{-6}/°C when measured between 23 and 400 °C. Solubilities tend to be high, but they are still within the commercial range. Many of these have very low deformation temperatures, i.e., the lowest temperature where stress between metal and ceramic may be relieved. Work continues on lowering the solubilities of these porcelains.

At least two dental companies have decided to experiment with gel route prepared frits. The gel route has potential for facilitating the introduction of nonradioactive phosphors to replace uranium in teeth.

Irradiation Effects From Neutron Activated Dental Materials
Subtask 8 of Task 12135

J. A. Tesk

A potential source of radiation exposure which has not received direct attention involves secondary radiation from dental restorations activated by primary exposure to neutrons. This could present an additional hazard for the civilian and military personnel surviving exposure to a neutron bomb, for reactor operators and experimentalists suffering accidental exposure, for cancer patients receiving intense localized neutron radiation therapy, and others occupationally exposed to neutron radiation. Accordingly, calculations were made to estimate the additional dose of radiation ($\beta + \gamma$) delivered to local oral tissues by neutron activated gold crowns. A primary 50 REM exposure was used as the baseline neutron exposure, as this clearly appears to be a complete survival dose for whole body exposure. For calculation purposes, a single gold crown of 2 grams was simulated by a disc 0.5 cm in radius and 0.14 cm thick located entirely on the buccal or lingual sides of a tooth to provide close approximation to soft tissue. We have concluded that secondary radiation doses from gold crowns activated by sublethal neutron fluences are comparable to the original dose from the neutrons. Results indicate that a 50 REM neutron dose would subsequently be accompanied by $\sim$ 30 REM. Higher primary neutron doses are followed by higher secondary doses (a high survival, whole body neutron dose of 200 REM is followed by $\sim$ 120 REM).

Dental or implant materials with major constituents behaving similarly to gold nuclei and irradiated by neutrons during cancer therapy will generate secondary doses comparable to the primary and must be duly considered. Long-range effects of partial irradiation of an organ are not well known. For the levels presented, concern appears warranted for minimizing exposure. This research has been summarized in an article to be submitted to Medical Physics.

Clinical and Laboratory Investigation of Dental Amalgams
Subtask 9 of Task 12135

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The reason for the progressive deterioration of amalgam restorations is a subject of intense interest although the theoretical understanding of this behavior is not well developed. Creep and corrosion are generally recognized as being important factors, but there is considerable controversy about the relative importance of these two factors, and it is possible that other significant factors have been overlooked.

Amalgam is a composite mixture of about six major constituents or "phases." The chemical and physical properties of such a mixture will depend on the properties of the individual phases, the percentage of each phase in the mixture, the size and shape of the crystals, and the properties of the interfaces between each phase. Thus, it is important to study the microstructures of each phase and to identify the tendencies for a chemical element to occur preferentially in certain regions of the microstructure. Elements such as tin, copper, manganese, and zinc are known to exhibit such behavior, and they produce important effects on the properties of the amalgam. These effects are being identified in a variety of experimental and commercial amalgams. An effort is then made to determine the relationships between the observed microstructure and the clinical behavior of the amalgams.

Currently, we are concentrating on the laboratory phase of the project. Dimensional changes are being observed for unrestricted specimens which have been stored in air at various temperatures for over three years. Seven pairs of alloys (zinc-containing paired with non-zinc-containing alloys of the same brand) have been under observation. All of the zinc-containing alloys made amalgams that continued to expand for the three years. The zinc-free amalgams all contracted. When one percent of powdered zinc was added to one of the non-zinc alloys, the change in dimension increased from -5 μm/cm for the non-zinc to +273 μm/cm. Thus, it would seem that zinc plays a role in the diffusion of mercury in hardened amalgam. This new knowledge of the role of zinc in the alloy may contribute to formula changes which could further improve the durability of amalgam restorations.

<u>Dental Enamel Chemistry and Preventive Dental Treatments</u>
Subtask 10 of Task 12135

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The objective of this project is to develop and apply fundamental information on the solubility and crystallographic structure of biologically important calcium-containing phosphate compounds to the development of improved dental caries preventive techniques. Important portions of this effort are concerned with (1) development of physicochemical models of the caries process to include insight into the mechanisms by which impurities and defects are incorporated into tooth enamel, and (2) application of solubility phase diagram analysis and kinetic data to the development of more effective enamel acid etch bonding treatments and improved topical fluoride procedures.

The structure of the following highly hydrated compounds has been determined: $MgNaPO^4 \cdot 9H_2O$ and $Ca_4AlSi(SO_4)F_{13} \cdot 12H_2O$. These studies on some of the first known examples in which the phosphate ions are completely surrounded with water molecules provide a new structural basis for understanding chemical properties of the physiologically important phosphate ion in aqueous solutions.

For clinical application of fluoride in the past we have used a two-step process in which the tooth was first treated with $CaHPO_4 \cdot 2H_2O$-forming solution, and then the $CaHPO_4 \cdot 2H_2O$ was converted to fluorapatite by a conventional fluoride solution. This procedure was shown to greatly increase the incorporation of permanently bound fluoride into enamel. We now have promising data for a new single step procedure which involves formation of $CaHPO_4 \cdot 2H_2O$ in the enamel. *In vitro* results showed that this procedure should be much more acceptable for clinical practice than a two-step procedure.

The use of relatively frequent mouth rinses with solutions containing low amounts of fluoride appears to be coming into favor over the use of infrequent treatments with concentrated solutions. We have made two *in vitro* studies in which a $CaHPO_4 \cdot 2H_2O$-forming step is incorporated into the fluoride rinse procedure. The results from these studies showed that the permanent fluoride uptake by the enamel was significantly increased over a method currently used.

A new dental cement system comprising primarily calcium phosphate has been developed. At present, the cement has a compressive strength only about one-half that of ZnO cement and requires a setting time of about 15 minutes. Both the strength and setting time are expected to improve as the materials and procedures are modified. This cement has many potential applications in dentistry.

Progress in utilizing ultra-micro techniques to simulate and study the decay process has been made in several areas. This technique has produced, for the first time, information on calcium, phosphate, chloride concentration changes, and the change in pH within enamel when the tooth specimen is undergoing a carious-like demineralization. This information provides important new insights into the mechanism of caries formation and has application to enamel remineralization processes as well.

Adhesion and Surface Coverage of Synthetic Polymers on Solid Substrates
Subtask 11 of Task 12135

R. E. Dehl, W. H. Grant

Two aspects of the adhesion of polymers to surfaces are of great importance in their many commercial applications as protective coatings: namely, (1) the energy of adsorption of individual polymer molecules on the surface, which determines the adhesive strength of the film, and (2) the extent of surface coverage by the polymer, which determines the effectiveness of the adherent film in protecting the underlying substrate from chemical attack. We are presently investigating both aspects of this important problem by the use of radiolabelled polymers to study the adherence of the film and by Auger Electron Spectroscopy to study the uniformity of surface coverage by the polymer.

One measure of the energy of attachment or adhesive strength of polymers adsorbed on solid surfaces is the rate at which they become detached when the polymer-coated substrate is placed in contact with a suitable solvent. The desorption rate is affected both by the free energy of attachment of each segment of the polymer molecule with the surface and by the number of attached segments per molecule. The results of previous NBS studies, using radiolabelled polystyrene to detect the amount remaining on the surface, indicate that the rate of desorption decreases with increasing molecular weight of the polymer and with the amount of polymer initially adsorbed. Further experiments are in progress to quantitate these observations by systematically varying the amount of polymer initially adsorbed, followed by a careful study of the amount remaining after selected intervals of desorption. In this way, we expect to learn whether the polymer molecules which first arrive at the surface have a higher adsorption energy than the later arrivals, and whether such variables as the solvent used to deposit the film and the time spent in depositing a given amount of polymer on the surface significantly affect the adhesive strength of the film.

Auger Electron Spectroscopy (AES) is a technique for determining the elemental composition of the topmost 5-10 nm of a solid surface. The AES probe samples an area of about 20-80 μm^2 and can be used to determine variations in the surface chemical composition, given this lateral resolution. Preliminary AES experiments indicate that we can detect changes in the average thickness of a polymer film on a metal substrate as we scan across the sample. We expect to use the AES technique to study the uniformity of polymer film thickness as it is affected by the molecular weight of the polymer, the mass of polymer adsorbed per unit area, the time required to adsorb a given mass of polymer, and the molecular volume of the polymer molecules in solution prior to their adsorption. By studying the effect of each of these variables, we expect to gain insight into the optimum parameters for applying uniform polymer coatings to solid surfaces.

Characterization of Porosity of Porous Implant Materials
Subtask 12 of Task 12135

R. E. Dehl, W. H. Grant, A. Bur, J. M. Cassel

The use of porous synthetic implant materials to serve as a scaffolding for the ingrowth of natural hard or soft tissue is a procedure utilized to stabilize selected medical implants. Characterization of the porosity of these materials is very important since the porosity governs their successful utilization. In cooperation with the Bureau of Medical Devices, Food and Drug Administration, a project has been initiated to survey published information and current commercial material specifications, perform void volume measurements on selected polymeric and composite materials by several alternative methods, and measure pore size distribution by optical intercept and mercury porosimeter techniques. In addition, the applicability of an experimental microparticle sieving technique, heretofore not applied to such systems, will be explored.

The accomplishments of this project's objectives will be of significance to the medical device industry, medical implant standards development, and ultimately, the users of porous implant materials.

Dental and Medical Materials Standards
Subtask 13 of Task 12135

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Active participation, from Task Force level to the role of Subcommittee Chairman, occurs in development of dental standards through ANSI MD 156, Dental Materials, Instruments, and Equipment, and ISO TC 106, Dental Materials and Services. Development of medical implant standards is assisted by serving in roles of Polymeric Materials Chairman and Task Force leadership in the efforts of ASTM F-4, Medical and Surgical Materials and Devices, and as Chairman, USA TAG ISO TC 150, Surgical Implants.

Investigation of Epitaxy Relationships Between $Ca_5(PO_4)_3OH$ and Other Calcium Ortho-Phosphates
Subtask 14 of Task 12135

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The purpose of this investigation was to examine possible epitaxies between $Ca_5(PO_4)_3OH$ (hydroxyapatite) and other calcium ortho-phosphates. These epitactical relationships are of interest for the following reasons: (i) $Ca_5(PO_4)_3OH$ may be considered as an idealization of the major inorganic phase in the human body, and its crystal chemistry obviously influences the properties of hard tissues, and (ii) epitactical relationships have been suggested to be important in explaining the apparent nonstoichiometry of $Ca_5(PO_4)_3OH$ and in the growth of biomineral in vivo.

Similarity in chemical content and periodicity of the chemical pattern between two planes in the component structures is an important requirement for epitaxy to occur under mildly forcing conditions. From the purely metric point of view, periodicity may be treated in terms of matching nets, one in each of the two components. In general, the metric fit of such nets will not be perfect, and the resultant misfit will be accomodated by lattice strain near the epitactical layer and/or by dislocations.

For the chemical aspects of epitaxy, structural features such as layers and corrugated sheets are prime candidates for the interfaces. Many structures contain layers in which the intra-layer bonds are strong and the interlayer bonds are weak. Especially in the case of inorganic salts, the atomic configurations in such layers will be relatively stable and, hence, can be expected to be found in more than one structure. The chemical pattern itself should not have a large motif, because this would have many structural details, and the probability of finding a similar motif in another compound would necessarily be low. From the above considerations, it follows that the most likely candidates for epitaxy-forming layers will be planes of low Miller indices of the form (100), (110), or (210), etc.

A filtering procedure for generating and quantitatively comparing possible cases of epitaxy and twinning in ionic compounds has been devised to provide quantitative criteria to evaluate the probability of epitaxy between compounds for which the crystal structures are known.

The two cornerstones of this procedure are:

(i) Generate and examine in a systematic, quick manner all possible cases of epitaxy and twinning that may occur.

(ii) Establish a relative probability of occurrence among the possible cases to delineate those requiring further study.

Our approach is completely general in that it can be applied to any substance that forms a crystalline phase. Generation of possible cases of epitaxy or twinning which are specified in terms of contact planes requires only unit cell dimensions. Further evaluation of these cases in terms of atomic correspondences requires atomic positions. The procedure was used to evaluate the possibility of epitaxy between $Ca_5(PO_4)_3OH$ and other calcium orthophosphates. For any two given lattices, pairs of nets which match dimensionally within prescribed limits are found and sorted in order of increasing mismatch. The crystal structural parameters are used to generate and match atomic patterns corresponding to each pair of nets. Pattern matching is done by comparing magnitudes of vectors describing the immediate environment of representative atoms in the two patterns. Atomic charges related by each vector are also considered. Use of the vector sets introduces the limitation that twinning involving reorientation in a contact plane cannot be distinguished from no reorientation. The procedure is general in nature and has been applied to the study of possible epitaxies between $Ca_5(PO_4)_3OH$ and $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, $Ca_4O(PO_4)_2$, $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$, β-$Ca_3(PO_4)_2$, and $Ca_5(PO_4)_2SiO_4$.

The highest probabilities for epitaxy are between $Ca_5(PO_4)_3OH$ and $Ca_8(PO_4)_6 \cdot 5H_2O$, $Ca_5(PO_4)_3OH$ and $Ca_4O(PO_4)_2$, and $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_2SiO_4$. Of these, the first is the most likely and is probably unavoidable under conditions where $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ is stable, and the last is the least likely. Possible epitaxies between $Ca_5(PO_4)_3OH$ and $CaHPO_4$ or β-$Ca_3(PO_4)_2$ are less likely than epitaxy between $Ca_5(PO_4)_3OH$ and $Ca_4O(PO_4)_2$.

Although $CaHPO_4 \cdot 2H_2O$ and $Ca(H_2PO_4)_2 \cdot H_2O$ had been suggested to be important in tooth mineralization, evaluation of the probability of epitaxy in these cases suggests that any deposition of these phases on one another forms incoherent films which then mechanically block access of the surrounding solution to the interior and that epitactical growth is not important. Therefore, among those cases considered, only the epitaxies $Ca_5(PO_4)_3OH/Ca_8H_2(PO_4)_6 \cdot 5H_2O$ and $Ca_5(PO_4)OH/Ca_4O(PO_4)_2$ appear likely to occur in practice.

Development of Improved Field Dental Composite Restorative Materials for Military Dentistry
Subtask 15 of Task 12135

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Current thrust of this continuing project is to provide guidelines to the Army regarding materials and techniques for addressing the problem of poor marginal adaptation that frequently occurs with composite restorative materials. Resultant marginal staining and leakage compromises the aesthetic advantages of these restorations and can reduce their service life.

The role of polymerization shrinkage, coefficient of thermal expansion, nature of filler, and properties of diluent monomers are being investigated. Efforts are being made to establish optimum minimum levels of viscosity-modifying diluent monomers that will produce adequate working characteristics and physical properties, while at the same time reducing the polymerization shrinkage that occurs on hardening. Radiotracer techniques are employed to ascertain leakage around class V restorations placed in extracted caries-free teeth.

MECHANICAL DURABILITY OF PLASTICS FOR DESIGN AND USE
Task 12136

Current trends are to use polymeric materials in applications where long-term mechanical reliability is critically important. Examples in areas of national concern include the increasing use of plastics and composites in transportation, in energy production, storage and distribution, and in medical implant devices. The lack of adequate test methods and data for evaluating long-term mechanical performance not only restricts applications, but also leads to overdesign which results in more expensive items and limits potential weight savings. The National Bureau of Standards has established joint programs on mechanical durability with other Federal agencies which are fostering the application of polymeric materials in areas of national concern. A joint program with the National Heart, Lung, and Blood Institute is aimed at developing accelerated test methodologies for evaluation of candidate biocompatible elastomers for use as bladders in circulatory assist devices. The Bureau of Medical Devices of the Food and Drug Administration supports an investigation of the relationships between the fine structure morphology of ultra high molecular weight polyethylene and the long-term mechanical properties of this material when used in medical implant devices. The mechanical performance of elastomeric seals in geothermal energy wells is of concern to the Department of Energy, and a joint effort is aimed at developing tests to estimate accurately the long-time behavior of seals in any condition of interest. In all of the above applications, there exists a need for test methods and standards to ascertain the physical limits of polymeric materials in various use environments. An outgrowth of a recent project with the Department of Transportation on the mechanical durability of plastic shipping containers has been the development of a new test for environmental stress cracking. This test has been reported to ASTM for evaluation as an improved standard method for stress-crack resistance.

Evaluation and control of materials parameters which affect long-term performance should lead to more durable materials and, hence, reliable performance for the intended service life. Task objectives are to identify and analyze principal failure mechanisms in polyethylene and elastomers under mechanical stress in the use environment. An integral part of these objectives is to determine the effects of chemical structure and mechanisms and fine structure morphology on mechanical properties. Activities in nuclear magnetic resonance, vibrational spectroscopy, electron and optical microscopy, as well as x-ray diffraction, are directed toward elucidating these effects.

Mechanical Durability of Polyethylene
Subtask 1 of Task 12136

J. M. Crissman, L. J. Zapas, G. M. Martin

In previous work done for the U.S. Department of Transportation, Office of Hazardous Materials Research, a failure mechanism was identified which is highly sensitive to the presence of a stress-cracking agent.

This mechanism is associated with the region of small deformations. In an effort to obtain a better understanding of this mechanism, experiments have been carried out on prestretched specimens. In the case of equal biaxial deformations under inflation, the interesting result is that this mechanism is highly influenced by the magnitude of the prestretch history and in such a way that the material becomes more stress-crack resistant. For example, a tenfold increase in lifetime was observed for specimens which were prestretched in air by twenty-five percent, were then left to relax, and subsequently were reloaded in the presence of stress-cracking agent. The eventual failure occurred at strains of twelve percent or less. After prestretching, the permanent set in the specimen was of the order of five percent or less. In all cases where the amount of prestretch was higher than the strain at failure, a significant increase in lifetime was observed. Further investigation is needed in order to understand this interesting behavior. In the case of uniaxial strain histories, the results of similar experiments were inconclusive.

In other work related to mechanical durability studies, we have shown that the phenomenon of neck formation, which occurs for uniaxial deformation histories, can be described by a mechanism leading to instability. Two different theoretical models (phenomenological) have been derived which lead to such an instability. To test the validity of either model, we have chosen for study two types of linear polyethylene having widely different molecular weights. One sample, having a molecular weight (Mw) of 192,000, exhibits necking at room temperature. The other polymer, an ultra high molecular weight material ($Mw > 2 \times 10^6$) does not show necking at room temperature, but extends homogeneously until fracture occurs. In both theories one should be able to predict from single step stress-relaxation experiments, carried out at different levels of strain in uniaxial extension, whether or not an instability occurs. Measurements made at very small deformations indicate that the behavior of the two polyethylenes is very similar. However, at deformations above eight percent, deviations in behavior occur which are consistent with both theories. Data have also been obtained for specimens of highly cross-linked polyethylene which have a density very close to that of the ultra high molecular weight linear polyethylene. The cross-linked material does show the phenomenon of necking. Therefore, experiments other than mechanical will be required in order to elucidate the differences between the two polymers and may lead to a better understanding of the phenomenon of neck formation from the molecular point of view. We know from previous experience that the incipient point of instability for linear polyethylenes occurs about a factor of two in time earlier than the time for which the neck becomes visible. One of the continuum theories predicts that the incipient point of instability will occur when the instantaneous jump modulus goes to zero. If the model is valid, then it should be possible to devise tests for nondestructive evaluation.

<u>Stress-Cracking Test for ASTM</u>
Subtask 2 of Task 12136

J. M. Crissman, L. J. Zapas, G. M. Martin

This project concerns the development of an improved test method for the determination of the stress-crack resistance of ethylene plastics.

Upon its completion, a description of the test method, as well as the appropriate statistical data will be submitted to ASTM Committee D-20.10 for their consideration. A preliminary report on the test method was presented to the ASTM Committee D-20.10 at their February meeting in San Diego, California. The test involves the use of a bent strip geometry, but differs from the current ASTM bent strip test in two important ways: the specimen is subjected to a constant applied stress and in the region of the bend, all specimens are maintained in the same geometry.

The failure time can be controlled to some extent by changing one or more of four parameters: the specimen thickness, the magnitude of the applied stress, the diameter of a metal cylinder (which determines the severity of the bend), and the temperature. In order to optimize these parameters, we are currently in the process of examining three different types of polyethylene which have widely different stress-crack behavior. Specimens of each polymer are being tested at two stress levels, two different cylinder radii, two different thicknesses, and at two or more temperatures. To determine the repeatability of the measurements, ten or more specimens are being tested for each set of parameters. Preliminary results indicate that two advantages of this test over the current ASTM bent strip test are improved repeatability and shortened testing time.

Ductile and Brittle Behavior of Polyethylene
Subtask 3 of Task 12136

A. Peterlin

Creep experiments on isotropic linear polyethylenes by Crissman and Zapas have shown that failure occurs by brittle fracture at both very small and very large loads. At intermediate loads, the materials are ductile and after necking may deform to a very large draw ratio before they break at a substantially higher tensile stress.

The lifetime, t_b, at both very small and very large loads may be described as a sum of the microcrack nucleation time, t_n, and the microcrack growth time, t_g, in the brittle range and the shear band growth time, t_s, after which the sample necks and deforms drastically. It turns out that the nucleus of the microcrack formed under the tensile load may produce a craze perpendicular to the local stress and a shear band at about 45 °C to this stress. The craze growth time is an exponential function of the negative stress, while the shear band formation time is proportional to the inverse stress. If the curves representing the lifetimes of the two deformation modes as a function of the applied stress intersect, then the intersections separate the brittle from the ductile regime of the sample under tensile load. As a rule, with increasing temperature the shear band formation curve moves more rapidly to lower lifetimes than the microcrack growth curve. This expands the ductile region at the expense of the brittle region. A decreasing temperature acts in the opposite direction so that eventually the two curves do not intersect at all, and the material becomes brittle in the whole load region.

In this consideration, one has completely neglected the highest load range where the deformation is so rapid that the material becomes substantially heated by the deformation work, and hence, tends to fail like a liquid.

<u>Spectroscopic Investigation of Failure Mechanisms in Polyethylene</u>
Subtask 4 of Task 12136

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The spectroscopic techniques of electron spin resonance and infrared spectroscopy are used to elucidate molecular mechanisms in polyethylene associated with exposure to γ-irradiation and with mechanical deformation and fracture. The irradiation studies, which have now been completed, not only gave information on the relationships between the number of new chemical species formed and the level of irradiation, but also provided a means of evaluating our experimental methods on samples in which the polymer molecules were not oriented during the exposure process.

Knowledge of molecular mechanisms associated with deformation and fracture in polymers is the main objective of the present work. Such information provides the basis for predicting long term performance from short time tests as well as insights into how the molecular composition may be changed to improve performance.

<u>Summary of Result on Irradiated Polyethylene</u>: Measurements of the concentrations of free radicals by electron spin resonance and of new chemical species by Fourier transform infrared (FTIR) were carried out on polyethylene specimens exposed to γ-irradiation at dosages from three to fifty Mrads, both in the presence and absence of oxygen. The improved signal-to-noise capability of the FTIR method permitted a direct comparison of the free radical concentration and the resultant concentration of new chemical groups. It was found that approximately ten carbonyl groups and two carbon-carbon double bonds were formed per free radical. These results are comparable with previous estimates and form the basis for an investigation of chemical species formed during mechanical deformation and fracture.

<u>Chemical Changes Accompanying Mechanical Deformation and Fracture</u>: The molecular mechanisms associated with mechanical deformation and fracture in polyethylene are elucidated through comparisons between FTIR spectra of undeformed and fractured specimens. Small variations in the concentrations of carbon-carbon double bonds, methyl groups, and carbonyl groups result from rupture of carbon-carbon backbone bonds and subsequent free radical reactions. These concentrations can be detected in difference spectra obtained through subtraction of the digital FTIR data. The ability to detect small concentration variations is enhanced by the superior sensitivity of the FTIR method over conventional dispersive infrared spectroscopy. The number and type of chemical groups formed are correlated with ESR measurements of the number of secondary radicals accompanying mechanical deformation and fracture.

Our results can be divided into two regimes associated with the rate of mechanical deformation. In one set of experiments, the polyethylene specimens in the shape of dumbbells were rapidly pulled in a tensile tester until ruptured, while in the other set specimens were allowed to deform under dead load conditions. In both cases, the deformed or fractured specimens were subsequently heated and pressed into thin sheets suitable for infrared analysis. In this manner, the difficulties inherent in comparing spectra of unoriented (undrawn) and oriented polyethylene which had plagued previous infrared studies of deformed and fractured polymers have been circumvented.

For the rapidly deformed specimens, we observed that the number of ketone groups <u>decreases</u> when compared to the reference polymer. This result is contrary to previous findings and suggests that bond rupture occurs preferentially near the ketone group and that subsequent reactions produce low molecular weight ketones which are volatilized during preparation of the specimens for infrared studies. Assuming that the ketone groups are preferentially located in the interlamellar regions, our findings support the notion that fracture occurs at lamellar interfaces.

When polyethylene specimens are slowly deformed, we observe the number of carbonyl and vinyl groups to increase, which is consistent with previously published reports. Experiments are in progress to substantiate these results on drawn polyethylenes to determine whether a relationship exists between the level of deformation and the concentration of each group.

<u>Fracture Mechanics of Polymers</u>
Subtask 5 of Task 12136

E. Passaglia

In April of this year, a new project on the fracture mechanics of polymers was begun. A complete review of the literature, concentrating on the effects of plasticity and viscoelasticity, is well along. A review paper in these areas is contemplated.

Technical work has concerned itself with the viscoelastic nature of the craze material at the tip of a slowly moving crack. Published results by Ward and his co-workers [1,2,3] and by Weidmann and Döll [4] show that the shape of the crazed region is quite accurately represented by the Dugdale model [5], which was developed for plastic yielding in metals. In this model, the stress in the yielded zone (which corresponds to the crazed region) is a constant and equal to the yield stress, with the length of the zone increasing as the applied stress intensity factor is increased. In the polymer case, however, it has been shown [4] that the stress in the crazed region is proportional to the applied stress intensity, with the length of the crazed region remaining constant. Moreover, other experiments [6,7] indicate that the craze material is viscoelastic and not plastic. We, therefore, have the unusual result of a theory developed for an elastic-plastic material accounting well for observations on a viscoelastic material.

This can, in principle, be explained if the relaxation of stress in the craze in the growing crack is compensated for by the elongation provided as the crack grows, in just such a manner as to produce a constant stress within the craze. Since the shape of the craze region is known from these results, it is, in principle, possible to determine the relaxation function for the craze material. For the linear viscoelastic case (which is probably too simple for this situation), this determination involves calculating the Laplace transform of the crack displacement, calculating from this the Laplace transform of the relaxation function, and then inverting this transform. The last step is known to be a delicate mathematical operation, so that while mathematical difficulties have been encountered, preliminary results show that the method is feasible.

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Physical Testing of Polymers for Use in Circulatory Assist Devices
Subtask 6 of Task 12136

R. W. Penn, G. B. McKenna, F. A. Khoury, G. W. Bullman

This project is directed to the development of accelerated physical testing procedures and to the evaluation of candidate elastomers for use in circulatory assist devices. The project is supported by the National Heart, Lung, and Blood Institute of the National Institutes of Health under contract #Y01-HV-8-0003. Three candidate materials are under study along with a standard butyl rubber. The three candidate materials are a polyolefin rubber, a urethane-silicone copolymer, and a segmented polyurethane elastomer. During this year, all of these materials have become, or are becoming, available in adequate supply.

We have obtained results from both uniaxial and biaxial testing with both static and dynamic stress histories. Our results show that in static uniaxial loading the butyl rubber is superior to the polyolefin at short times (high stresses) but that this behavior reverses at long times (low stresses). Under dynamic (fatigue) loading, the failure times decrease with increasing test frequency but not rapidly enough to say that the samples fail after a constant number of cycles. Statistical analysis of the failure data shows that there is greater variability in the failure times for the polyolefin rubber than for the butyl rubber in all tests in which a comparison can be made.

Biaxial fatigue test results show that the urethane-silicone copolymer lasts longer than the polyolefin rubber, which lasts longer than the butyl rubber when they are compared at the same reduced pressures. For both the polyolefin rubber and the butyl rubber, the dependence of lifetime on stress is the same in static and fatigue loading. The butyl rubber in both cases shows a higher stress dependence. In the case of both rubbers, the variability in the failure times is greater in static testing than in dynamic testing. Data for the butyl rubber and preliminary results for the urethane silicone copolymer from biaxial fatigue tests at 23 and 37 °C reflect activation energies for the failure process of 22 kcal and 25 kcal, respectively.

Creep data under uniaxial loading have been obtained for all four elastomers. Creep rates range from 1.7 percent per decade of time for the segmented polyurethane elastomer to four percent per decade for the polyolefin rubber.

Examination of the urethane-silicone copolymer by optical microscopy shows heterogeneities on a coarser scale than has been previously reported. These structures consist of flattened spheroids with their short axes perpendicular to the plane of the sheet. Their sizes parallel to the plane of the sheet vary from a few micrometers up to about 30 μm.

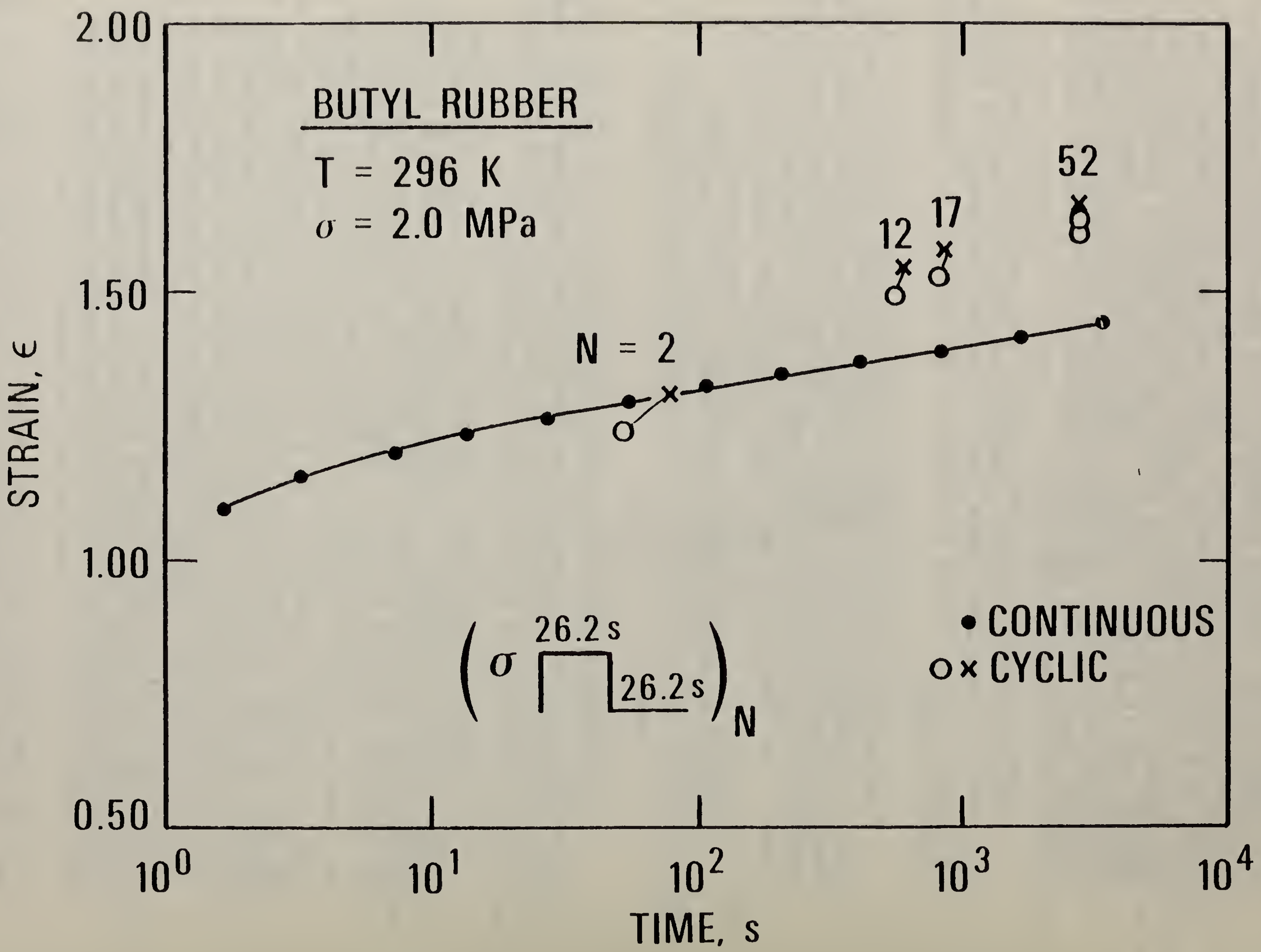
<u>Response of Carbon Black Filled Rubber to Cyclic Loading</u>
Subtask 7 of Task 12136

G. B. McKenna, L. J. Zapas

We have been examining the deformation behavior of a carbon black filled butyl rubber in view of the Bernstein-Kearsley-Zapas (BKZ) constitutive equation. Failure behavior has been studied within the context of cyclic creep and a cycle shifted failure envelope.

For materials which follow BKZ type behavior, the single step stress relaxation response is a lower bound on the cyclic stress relaxation behavior, and the single step creep response is an upper bound on the deformations obtained in cyclic creep. In the responses observed for the carbon black filled rubber, we found that upon cycling the material, the creep and stress relaxation responses were outside these bounds. (See, for example, figure 1). We also found that the softening was more emphatic in cyclic creep than in cyclic stress relaxation. Further work needs to be done in order to understand these results for materials which are nearly elastic in constant stress or strain histories. We have also found that the material creep response in constant load experiments is stiffer than that predicted from the BKZ constitutive equation. It is suggested that an adequate description of the material behavior might be obtained by developing a theory similar to the BKZ theory which includes competing effects of stiffening in creep and softening under load-unload cycling.

In studying the cyclic creep behavior of the butyl rubber, we found that the creep rate is dependent upon the waveform and frequency of the test. Also, unlike the case of static creep, the creep rate under the


BUTYL RUBBER
T = 296 K
σ = 2.0 MPa
N = 2
12
17
52
26.2 s
26.2 s
N
● CONTINUOUS
○ × CYCLIC
STRAIN, ϵ
2.00
1.50
1.00
0.50
TIME, s
10^0
10^1
10^2
10^3
10^4

cyclic loading is a function of the stress level. An interesting point which arises in examining the cyclic creep data is that the square waveform load-unload cycle which had a test frequency of 0.02 Hz showed nearly the same behavior as the sinusoidal load-unload cycle at 0.01 Hz. This would indicate that stress softening occurs due to cycling but is independent of the rate of load application. The amount of stress softening depends upon both time and cycles. This can be seen from the fact that the amount of stress softening per cycle increases with decreasing frequency, and the stress softening per unit time increases with increasing frequency.

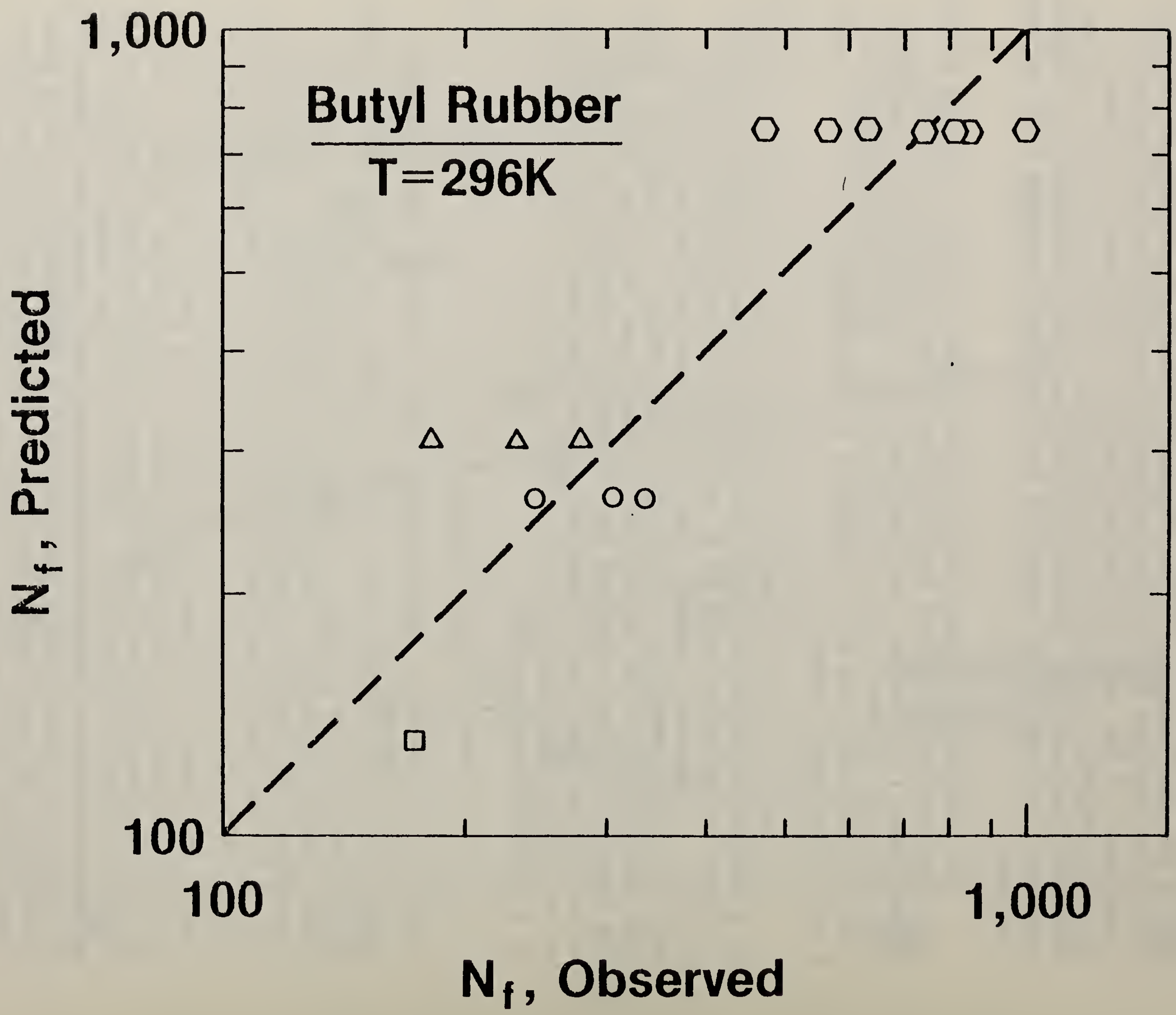
The lifetime of carbon black filled rubber in cyclic loading depends upon the test frequency and the waveform of the loading cycle (e.g., square wave vs sine wave). We have been able to use cyclic creep data combined with the notion of a shifted failure envelope to account for the frequency and wave form dependence of the fatigue lifetime of carbon black filled butyl rubber.

In simple loading histories, failure of rubbers is readily described by a failure envelope for which the locus of stress at break vs strain at break can be represented as a unique curve independent of stress history. In general, however, the failure envelope can be dependent upon the loading history. In addition, the amount of change may depend upon the stress. Since in our cyclic creep experiments we found that the amount of stress softening was relatively independent of waveform, and all of our tests were conducted at the same peak stress (5.5 MPa), we can express the change in the failure envelope due to cyclic loading by a shift factor a_σ. Then

$$\varepsilon_{bc} = a_\sigma \, \varepsilon_{bo} \tag{1}$$

where ε_{bc} is the strain at break under cyclic loading, a_σ is a shift factor, which may depend on the level of stress, and ε_{bo} is the failure strain (at the same stress) in a simple deformation history (i.e., creep, stress relaxation, constant rate of deformation). With this assumption, the same shift factor should permit prediction of all of our cyclic failure data by extrapolation of the cyclic creep strain data to the ε_{bc} determined from eq. (1) and one set of the failure data. The results are shown in figure 2 in a plot of the predicted number of cycles to failure vs the observed number of cycles to failure. The points show the data, and their distance from the dashed line gives the deviation from the predictions. Given the limited number of data, the agreement is good. The observed deviations could arise from variability in the cyclic creep data, a possible history dependence (which we have ignored) of the amount which the failure envelope shifts, as well as the normal amount of variability in the number of cycles to failure in fatigue type testing.

Work is continuing in our study of the effects of cyclic loading on creep and failure of carbon black filled rubbers. An effort is being made to find an appropriate constitutive law to include the effects of stiffening in creep and softing due to cycling of these materials.


Butyl Rubber
T=296K
1,000
100
100
1,000
N_f, Predicted
N_f, Observed

Experiments are being conducted to assist in this development. Experimental work is also continuing to explore in more detail the applicability of the cycle shifted failure envelope to the description of fatigue lifetime of filled rubbers.

<u>Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene</u>
Subtask 8 of Task 12136

G. B. McKenna, F. A. Khoury, J. M. Crissman

The starting material used in the manufacture of the polymeric components of orthopedic prostheses is ultra high molecular weight polyethylene (UHMWPE) in its nascent state (i.e., as polymerized). The devices made from UHMWPE are fabricated in one of two ways: a) they are machined from rods or blocks prepared from the raw polymer (usually by compression molding) or b) they are molded directly from the nascent polymer powder into the desired shape. In clinical use, the long-term performance of implants made from UHMWPE is determined by time dependent phenomena such as creep, fatigue, and wear. The manner in which these phenomena depend upon the thermal history and resultant morphology is not well understood.

Under contract with the Food and Drug Administration (FDA) Bureau of Medical Devices, we are studying the relationship between morphology and the mechanical properties of UHMWPE. Our work has three specific goals:

(1) To determine the influence of polymer morphology on the time dependent mechanical properties of UHMWPE and to identify thereby the fine structural parameters which significantly affect long-term performance.

(2) To generate data in the areas of compressive creep, stress relaxation, and time dependent failure behavior which will be useful as a basis for evaluating the future and current devices made from UHMWPE.

(3) To devise measurement techniques which will be relevant to the development of standard test methods for characterizing the time dependent mechanical properties of implants fabricated from UHMWPE.

During this first year of the project, we have focused our efforts in three areas: (a) developing the molding capabilities and techniques to fabricate samples of UHMWPE in a reproducible manner; (b) characterization of the morphology of the UHMWPE polymer as received after molding and after deformation and failure; and (c) characterization of the time dependent mechanical behavior of UHMWPE.

We have developed a technique for fabricating sheets of UHMWPE using a vacuum mold. These sheets are used for uniaxial and equibiaxial test specimens. We are currently developing a technique for fabricating cylindrical specimens for compression testing.

Morphological characteristics of the UHMWPE raw polymer and of the fabricated sheets are being characterized using scanning electron microscopy, wide, and small angle x-ray diffraction, optical microscopy, and differential scanning calorimetry. Initial work has shown that the raw polymer has a grain-like structure which is carried over into the molded sheets. Also, the melting point of the raw polymer is significantly higher than that of the molded sheets, which indicates a higher degree of crystallinity in the raw polymer. X-ray diffraction patterns from samples which have been drawn to failure and then released show that there is considerable permanent orientation. Small angle x-ray diffraction shows changes occurring in the lamellar texture due to the deformation process.

The uniaxial creep and failure behavior of the UHMWPE is being characterized. Room temperature testing gives the interesting result that UHMWPE does not neck, but rather deforms and draws homogeneously to failure. This is unlike the behavior of lower molecular weight polyethylene. Our test results to date indicate that the time to failure in uniaxial testing is shorter for continuous loading than it is for zero-tension cyclic (fatigue) loading at 0.002 Hz. Further testing needs to be performed to substantiate this result and to determine effects of test frequency on lifetime.

The Crystallization, Morphology, Deformation, and Orientation of Polymers
Subtask 9 of Task 12136

F. A. Khoury, L. H. Bolz

Investigations of the morphology of crystalline polymers during the past year have been mainly in the two areas outlined below.

The Habits of Polyethylene Crystals Grown From Solution at High Temperatures: The objective of this investigation is to determine the effects of crystallization temperature, molecular weight, and polymer concentration on the morphology of chain-folded polyethylene crystals grown from solution at temperatures which approach and overlap the temperature range (~ 118-130 °C) in which the polymer crystallizes isothermally in the form of axialites or spherulites upon cooling from the molten state.

In an earlier experimental study, polyethylene fractions (molecular weights 11,400-100,500) and unfractionated ultra high molecular weight polyethylene (molecular weight ~ 4.5 x 10^6) were crystallized from 0.01 percent solutions in various solvents in the temperature range 95 to 115 °C. Distinct trends in the effects of molecular weight and undercooling on the lateral growth habits of the crystals were observed. During the past year we have attempted to grow crystals from solutions of the same polymer concentration (0.01 percent) at even higher temperatures. This has been achieved with a fraction of molecular weight 28,900, crystals of which were grown at temperatures up to 120 °C using docecanol as a solvent.

In an attempt to deduce the nature of the conformation (e.g., tent-like or variously curved) of the various species of polyethylene crystals we have grown between 95 and 120 °C, a study is under way in which scanning transmission electron microscopy and small-area (diameter ~ 0.4 μm) electron diffraction are being used to determine the details of the inclination of the chain stems relative to the surface of the lamellae. Of particular interest in this connection are crystals which, earlier results indicated, have asymmetric (apparently S-like) cross-sectional shapes when viewed along the b-axis direction. Our present aim is to determine how widespread and varied is the manifestation of this feature among the various types of polyethylene crystals we have grown. We believe that such cyrstals will serve as useful models for the constituent twisted lamellae in polyethylene spherulites grown from the melt at high undercoolings. It has recently been reported in the literature that the constituent lamellae in such spherulites, which lamellae are oriented with their b-axis parallel to the spherulite radius, exhibit S-shaped cross-sections when viewed along that direction [R. H. Olley, A. M. Hodge, and D. C. Bassett, J. Poly. Sci., Poly. Phys. Ed., 17, 627 (1979)].

The Morphology of Compression Molded Ultra High Molecular Weight Polyethylene: Aspects of the morphology of compression molded ultra high molecular weight polyethylene (UHMWPE, molecular weight ~ 4.5 x 10^6), and the fine structural changes induced in molded sheets of this material as a result of uniaxial deformation have been examined. This work is part of a new project which is sponsored by the FDA, and whose objectives are to characterize the mechanical properties of UHMWPE (G. B. McKenna and J. M. Crissman) and to examine the relationships between these properties and the morphology of the polymer. These relationships, which bear importantly on the durability of products made from UHMWPE, are of particular interest to the FDA because numerous components of artificial orthopedic implants (e.g., hip cups, tibial plateaux) are made from this polymer.

Sheets of UHMWPE which were compression molded at temperatures in the range 190 to 230 °C and were subsequently cooled slowly to room temperature, all exhibited a memory of the grain-like character of the as-polymerized raw polymer powder which is the usual starting material from which the implant components are manufactured. The density of the sheets was 0.936 gm/cm^3. Examination under the optical microscope, with cross polarizers, of thin cross-sections cut from the sheets revealed a heterogeneous distribution of birefringent structures of varying sizes. In some regions the sections had a very fine granular appearance. In others, larger structures were seen, the largest of which were distinctly spherulitic. Small angle x-ray diffraction patterns obtained from the sheets did not exhibit any distinguishable diffraction ring. This is either because the thickness of the lamellae was greater than the largest spacing (~ 300 A), which can be resolved in the present instrument, or because there is a large distribution in the thickness of the lamellae due to the fact that the polymer was not crystallized isothermally.

Dumbbell shaped samples cut from sheets molded at 200 °C were subjected to uniaxial extension at 1 mm/min at 23 °C, 37 °C, and 70 °C. In contrast with lower molecular weight linear polyethylene (e.g., molecular weight $\leq$ 200,000) the samples deformed uniformly and did not exhibit any necking even up to the breaking point. Current experiments are aimed at determining the recovery of samples from deformation at 23 °C, 37 °C, and 70 °C to various strains below the breaking strain. Low angle and wide angle x-ray diffraction and scanning electron microscopy are being used in an attempt to determine the nature of the permanent and recoverable changes in orientation and fine structure resulting from deformation to various strain levels. Structural changes resulting from stress relaxation will also be examined.

Polymeric Sealants for Geothermal Energy
Subtask 10 of Task 12136

E. A. Kearsley

The Department of Energy (DOE) envisions that within a matter of decades the exploitation of geothermal energy resources will be making a substantial contribution to our national energy needs. However, in order for this to be accomplished, it is necessary to stimulate several associated technologies. The Division of Geothermal Energy of DOE has accordingly requested help in developing tests of polymeric materials to screen likely candidates for use as geothermal sealants. Since there are many forms of seals used in the drilling and production of geothermal wells, and down-hole environments vary considerably among the different well locations, it is not possible to specify reasonable requirements for geothermal sealants in general. The most interesting and energetically important wells are potentially those with ambient down-hole temperatures greater than 260 °C and with strongly corrosive reducing (rather than oxidizing) atmospheres. The sealant materials should perform (frequently this means maintaining large elastic stresses for fixed deformations) under these demanding conditions for time periods ranging from hours for well-drilling sealants to months or years for production seals. Current technology for such seals is largely based on developments for the petroleum industry and is, consequently, adapted to lower temperatures and less corrosive conditions.

At present, various ad hoc lifetime tests are used by designers of geothermal equipment to test specific seals under conditions simulating the intended use. Such tests are very specialized and inconvenient. Failures of the seals are observed to occur either because the sealant hardens and eventually cracks or because the sealant softens and flows. The program on geothermal sealants in the Polymer Science and Standards Division aims at a more fundamental test which gets at the causes of this behavior so that the results can be used to design seals for whatever configuration or geothermal environment is needed. This is to be achieved by measuring the rates of formation and of breaking of bonds (cross-links or equivalent) affecting the elastic properties of sealant materials aging under controlled conditions. With information on how these rates depend on the parameters of the down-hole atmosphere, it should be possible to estimate accurately the long-time behavior of seals of any geometry (e.g., packer seals, o-rings, chevron seals, etc.) in any conditions of interest.

The customary way of measuring rates of cross-link breaking and forming is that developed by Tobolsky et al., to study oxidative degradation of rubber. In that method, two sets of measurements are required: (1) the stress relaxation of material aging while deformed and 2) the change in elastic modulus of material aging in an undeformed configuration. The latter data can be collected rather routinely, but stress relaxation is an inconvenient experiment, particularly under conditions corresponding to geothermal down-well atmospheres. Consequently, we have worked out the theory of a method to substitute permanent-set data for the stress relaxation data needed for the Tobolsky method. The theoretical work for this is completed, but there remains the task of establishing the most practical experimental methods of making the measurements.

Currently, the technique is being evaluated using simulating temperatures but not simulated geothermal fluids. The test samples are sealed in evacuated glass tubes during aging (at 260 °C) to avoid oxidation, since geothermal atmospheres are normally reducing rather than oxidizing. The conditions necessary to simulate complete relaxation prior to the measurement of permanent-set are still not completely known. Concurrently, an apparatus is being constructed to age samples in more realistic conditions, that is, in water compressed up to pressure of 5000 psi at temperatures up to 350 °C. Such conditions may induce hydrolysis of the sealant materials, thus affecting bond stability.

Characterization of Polymeric Solids by ^{13}C NMR
Subtask 11 of Task 12136

D. L. VanderHart, S. J. Kryder

High resolution ^{13}C NMR of solid samples has been greatly aided by the recent development of magic angle sample spinning (MASS) together with the technique of high-power proton decoupling. With MASS, ^{13}C NMR lines in solids appear at their isotropic chemical shift positions, just as they do in liquids, thereby enabling one to separate resonances corresponding to chemically different carbons. In the absence of MASS, ^{13}C lineshapes are much broader, and different ^{13}C resonances are likely to show a modest to severe overlap. Nevertheless, these lineshapes in chemically simple materials, e.g., polyethylene (PE), contain interesting orientational information, and as discussed below, we have made use of such measurements to follow the orientational behavior of noncrystalline PE chains during annealing. For the last two years MASS capability has also been available on a spectrometer with a magnetic field of 1.4 T. This past year, however, a 4.7 T superconducting-solenoid spectrometer was installed as an NML facility. This spectrometer, although principally equipped for liquid-state NMR, also has MASS capability in conjunction with ^{13}C NMR in solids, and this facility is expected to become a more significant instrument for our program because of its higher sensitivity.

Studies of Orientation in the Non-Crystalline Regions of Drawn Polymers: It has been demonstrated here that it is possible to separate ^{13}C signals in polyethylene (PE) arising from chains having preferentially high mobility relative to crystalline chains. Furthermore, it is possible to analyze the distribution of orientations. These studies are being extended to include ultra high molecular weight drawn PE whose macroscopic drawing characteristics (maximum draw ratio, lack of necking) are quite distinct from the lower molecular weight samples. Further, if samples can be obtained, it would be of interest to examine Pennings-type solution-shear-aligned PE fibers because the morphology is established by crystallization in shear flow rather than by deformation. Thus, one might expect more extended chain material but perhaps a reduction of entanglement-related connectivity. There is current effort to extend this method for measuring non-crystalline orientation to polyethylene terephthalate (PET), which is a commonly used commercial fiber. In PET, preliminary experiments have shown promise that the CH_2 resonance can be used to determine orientation in the non-crystalline region. But PET is more complicated than PE in that the ratio of relaxation times (molecular mobilities) between the crystalline and non-crystalline phases is expected to be smaller than in PE; furthermore, there is some argument about whether crystallinity means organized molecular packing or merely all-trans chains. Further work on these substances will also involve correlations with mechanical properties as well as the acquisition of a non-spinning probe for the 4.7 T NML spectrometer to take advantage of its higher sensitivity. Use of non-spinning ^{13}C NMR as a comparative tool in monitoring orientation in glassy polymers below Tg should also be investigated.

Resolution in ^{13}C MASS Spectra in Polymers: This work is aimed at evaluating the capabilities of the ^{13}C MASS technique for (1) studying relaxation of individual carbon sites, (2) studying tacticity and/or conformation in the solid state, (3) using the method as an analytical tool, and (4) using linewidths as a source of information about molecular motion or molecular packing.

We are currently in the final stages of preparing an extensive manuscript on the subject of resolution in the ^{13}C NMR of hydrocarbons using MASS. One result of this study is that molecular motion in the mid-kilohertz region produces overwhelming broadening for protonated carbon resonances. Thus, if one wishes to perform analytical measurements on a sample and needs best-available resolution, the ability to vary temperature and move to a region where motions do not create inordinate broadening is highly desirable. Another outgrowth of looking into the resolution question is the recognition that solid polymers often exhibit chemical shift dispersions and discrete magnetic inequivalences which are unique to the solid and which are averaged in solution. Chemical shift dispersions can arise from variation in the packing of chains. This is a difficult problem to address theoretically because of the complex nature of the chemical shift expressions. This problem was addressed experimentally by looking at changes in resonance positions of the interior methylene resonances in the alkanes as a function of crystal structure. The n-alkanes are found to have four crystal habits, and corresponding resonances were found to range over 1.3 ppm. Thus, it was concluded that packing variations, particularly in glassy polymers, can account for chemical shift dispersions of the order of 1-2 ppm and that no conformational variations need be invoked to explain such dispersions. This is an important perspective to have gained.

With respect to discrete magnetic inequivalencies, consider crystalline isotactic polystyrene which shows six distinct aromatic carbon resonances, whereas only four are observed in solution. Variable temperature studies of the collapse of such inequivalences in the solid would give very specific information about the frequency and nature of molecular motion, e.g., initial collapse from six to four resonances in polystyrene would correspond to rotation of the ring about the aromatic-aliphatic C-C bond direction at a frequency closely related to the splitting. Therefore, one of the badly needed instrumental modifications required is to design and build a variable-temperature MASS probe. It is not a simple matter to design such a probe without sacrificing sensitivity. Nevertheless, it is a high priority item to equip both the high and low field instruments with such a probe, in order to:

(1) move away from undesirable temperatures to get improved resolution,

(2) study temperature dependent motions in polymers,

(3) improve quantitation (will be discussed) for analytical applications, and

(4) study conformational equilibria.

<u>Quantitation in ^{13}C NMR Spectra of Solids</u>: If a broad-band pulse is applied to ^{13}C spins having equilibrium Boltzmann populations, resulting NMR spectra are quantitative in the sense that each ^{13}C nucleus appears to make an equal contribution to the total signal. Because ^{13}C signals are inherently weak and because many carbons have no directly bonded protons (thereby making their relaxation times long), the method just described is seldom used to generate ^{13}C signals. Rather, cross-polarization techniques are usually used in which ^{13}C magnetization is transferred from protons to carbons. While this method generally enhances the ^{13}C signals over the first experiment by a factor of 3 to 4, and further, allows one to repeat scans in a time determined by the proton rather than slowest carbon relaxation, the quantitativeness of the resulting spectra is no longer assured. On theoretical grounds, distortions of true intensities can be expected both when molecular motions are in the mid-kilohertz range and when molecules are isotropically tumbling and translating. This general area deserves more attention in polymers, particularly in blends, copolymers, or multiphase polymers. Such distortions are observed in the spectra of PE, as well as polycarbonate and polyethylene oxide. For exploring the problem of quantitation, temperature is an essential variable. A particular area where quantitation problems are likely to be severe is analysis of extent of curing, e.g., in dental composites.

<u>Impact and Use of the High Field NMR</u>: There is no doubt that sensitivity per scan is higher at high field, but relaxation times for slowly moving molecules may increase tenfold with respect to the lower field, thereby making relative sensitivities comparable. A perspective must be developed. Resolution using MASS at high versus low field is

still an open question. It is only a rare case where resolution dramatically improves; nevertheless, a more complete perspective must be developed here in order to optimize spectral information.

Acoustic Emission of Crazing Polymers
Subtask 12 of Task 12136

A. Peterlin, R. E. Green[1], B. B. Djordjevic[1], R. C. Murphy[1]

[1]Johns Hopkins University

After repeated attempts to observe acoustic emission in strained poly(methyl methacrylate) (PMMA), we have concluded that the emission occurs in the millisecond range where the noise background of the stretching machine completely masks the acoustic emission. Therefore, a statically bent PMMA specimen was observed with a reflected laser beam during the wetting of the bent surface by a droplet of benzene. The formation of crazes and vertical displacements of the surface of the bent slab of PMMA were observed. Indeed, the duration of the pulse, detected by the vertical motion of the polymer surfaces reflecting the laser beam, turned out to be in the millisecond range. Time extension of the pulse has shown a fine structure which is mainly caused by the interference of the primary signal with the waves reflected at the fixed ends of the bent slab. The reflections distort the acoustic emission signal to such an extent that its time dependence cannot be determined.

The optical method has definitively shown that the craze forms relatively slowly in about 1 ms and that it forms in a great many single steps of almost equal amplitude. Concurrently, the bent slab assumes a more bent position as a consequence of the elongation of the convex bent surface by the newly formed craze. Since the new position is obtained by damped oscillations which displace the reflecting surface of the bent slab vertically, the laser signal also records this movement which has no direct connection to the acoustic emission of the craze.

Non-Linear Elastic Behavior of Polymeric Materials
Subtask 13 of Task 12136

E. A. Kearsley, G. B. McKenna, L. J. Zapas

The theory of finite deformations of an elastic medium is often used with the added restriction of incompressibility of the medium. This restriction makes possible the solution of several classes of problems in terms of an unspecified strain-energy potential; however, it excludes the possibility that the elastic material properties depend on pressure. To make possible the use of these solutions in cases where material properties are pressure dependent, we have derived a different form of the theory. Through a Legendre transformation, the equations of finite elasticity of a compressible medium were formulated in terms of an elastic potential whose independent variables are pressure and shear rather than the usual deformation invariants. This elastic potential has no explicit dependence on volume change. Rather, the two derivatives of the potential are equal to the stress deviator and the volume change. The form of the resulting elasticity equations makes clear the mechanical effects of introducing a large ratio of bulk modulus to shear modulus into elasticity theory and leads to a theory of an (almost) incompressible medium for which the shear modulus depends upon the isotropic part of the stress. Through the elastic potential, some specific relations among the pressure coefficients of the mechanical moduli and the change of volume with deformation can be derived. These relations are accessible to experiment, and they suggest an interesting method of elucidating the effects of pressure on the mechanical behavior of natural rubber.

Our recent work with the theory of rubber elasticity has shown that the strain-energy function for elastomers (which determines the non-linear elastic behavior) may be measurable from experiments simpler than hitherto thought possible. However, the method depends upon the strain-energy relation having a special form (the Valanis-Landel form). Although some data already in the literature support this requirement, there are also some published data which raise questions about its validity. The point needs clarification. Experiments are under way to test the validity of the Valanis-Landel form through an experiment on simultaneous extension and torsion of cylinders of elastomers.

Non-Linear Viscoelastic Behavior of Poly(methyl methacrylate)
Subtask 14 of Task 12136

G. B. McKenna, L. J. Zapas

We have conducted single step stress relaxation experiments on cylinders of poly(methyl methacrylate) (PMMA) where we measured torque and normal force responses as functions of time and angle of twist. By assuming that torsion is an isochoric motion and that volume effects are separable, we obtained [1] isochronal values for the derivatives of the strain potential function, $\partial W/\partial I_1$ and $\partial W/\partial I_2$. Our results showed that $\partial W/\partial I_1$ is negative, while $\partial W/\partial I_2$ is positive and greater in magnitude than $\partial W/\partial I_1$. These findings provided the possibility of explaining the phenomenon observed by Sternstein and Ho [2] that the single step stress relaxation responses of PMMA are different in torsion and in simple extension. Specifically, the time rate of decay of stress is significantly higher in torsion than in extension. This phenomenon was observed at small strains where the stress responses in torsion and extension were linear in the appropriate strain measures.

Using a form of the viscoelastic strain potential function similar to the Valanis-Landel [3] form of the strain energy function for elastic materials, we calculated the response in simple extension from our torsion-normal force determined values of $\partial W/\partial I_1$ and $\partial W/\partial I_2$. Although we obtained good agreement between our calculated and our observed extensional behaviors, we could not account fully for the observations of Sternstein and Ho [2].

Table 1 shows some isochronal data for $\partial W/\partial I_1(t) = W_1(t)$ and $\partial W/\partial I_2(t) = W_2(t)$ for measurements made on PMMA in the form of both annealed rod and unconditioned tube. We remark on three things about these data. First, $W_1(t)$ is negative while $W_2(t)$ is positive and of greater magnitude than $W_1(t)$. This is different from the behavior usually observed in rubbers and polymer melts, where W_1 is usually positive and larger than W_2. Another observation we can make is that $W_1(t)$ and $W_2(t)$ exhibit different time dependences.

Also, the time dependence of the modulus, $2(W_1+W_2)$, is different from that of either $W_1(t)$ or $W_2(t)$. (At the limit of small strains, i.e., in the linear range, the modulus $G(t) = 2[W_1(t) + W_2(t)]$). Finally, the magnitude of $W_1(t) + W_2(t)$ is different for the two different PMMA's. This is not attributable to the geometry difference but may be due to the differences in both source and thermal histories of the materials.

Table 1

Some Isochronal Values of $W_1(t) + W_2(t)$, $W_1(t)$ and $W_2(t)$ for PMMA

Annealed Rod

		W_1+W_2	W_1	W_2		W_1+W_2	W_1	W_2
	ΨR	GPa	GPa	GPa		GPa	GPa	GPa
1.64s	0.00252	0.63	-2.19	2.82	1678s	0.488	-1.94	2.43
	0.00946	0.59	-1.98	2.57		0.456	-1.39	1.84
	0.0126	0.58	-1.82	2.40		0.442	-1.15	1.60
	0.0252	0.53	-1.10	1.63		0.379	-0.616	0.995

Unconditioned Tube

		W_1+W_2	W_1	W_2		W_1+W_2	W_1	W_2
1.64s	0.0095	0.48	-1.24	1.72	1678s	0.36	-0.79	1.15
	0.012	0.46	-1.24	1.70		0.35	-0.76	1.11
	0.016	0.45	-1.14	1.59		0.33	-0.65	0.98
	0.0208	0.44	-0.96	1.40		0.31	-0.47	0.78

From these data we determined isochrones for the viscoelastic V-L function $w'(\lambda)$ for both the rods and tubes. From the $w'(\lambda,t)$ we then calculated $\sigma_{11}(t) - \sigma_{22}(t)$ for simple extension. The agreement between the calculations and the experiments was within the uncertainty for our values of $w'(\lambda,t)$. (This uncertainty in the small strain region is approximately ± 15 percent due to the large uncertainties in the normal stress measurements in this region.) Of greater interest is the comparison of the relaxation rates in extension and torsion.

Table 2 summarizes our results and those of Sternstein and Ho [2]. The relaxation rates given in table 2 are calculated from the slopes of log (stress) vs log (time) plots. There are several things about these data which need to be discussed. First, Sternstein and Ho obtain greatly different rates of relaxation in extension and torsion (-0.0195 vs -0.0329) at strains of $\varepsilon = 0.005$ and $\gamma = 0.01$, respectively. Our data in torsion show a slightly higher relaxation rate than theirs for $\gamma = 0.01$ which increases as γ increases. Also, our data indicate that there is little difference in relaxation rates in extension and torsion at strains less than $\varepsilon = 0.02$ and $\gamma = 0.04$. But at strains of $\varepsilon = 0.02$ and $\gamma = 0.04$ and higher, we find that there is a more rapid torsional relaxation rate than extensional relaxation rate (-0.058 vs. -0.047). We are currently planning experiments to further elucidate these differences and perhaps account for the differences between our data and those of Sternstein and Ho.

Table 2

Relaxation Rates for PMMA for Different States of Deformation

Strain	Relaxation Rate[1]			
	Tension Predicted	Observed	Torsion[2]	Simple Shear[3]
Data of Sternstein & Ho[1]:				
$\varepsilon = 0.005$; $\gamma = 0.01$	--	-0.0195	-0.0329	--
Unconditioned Tubes:				
$\varepsilon = 0.01$; $\gamma = 0.02$	-0.0397	-0.0384	-0.0377	-0.0450
$\varepsilon = 0.02$; $\gamma = 0.04$	-0.051	-0.047	-0.0581	-0.0634
Annealed Rods:				
$\varepsilon = 0.005$; $\gamma = 0.01$	-0.0370	-0.0319	-0.0345	-0.0395
$\varepsilon = 0.0075$; $\gamma = 0.015$	-0.0371	-0.0335	-0.0360	-0.0420

[1]Calculated from the slope of log (stress) vs. log (strain) plots. Rate is per decade of time.

[2]Observed experimentally. γ is the maximum strain in the tube or rod.

[3]Calculated from values of W_1 and W_2 obtained from torsion-normal force measurements. γ is the shear strain.

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Retractive Forces in Drawn Low Density Polyethylene During Annealing
Subtask 15 of Task 12136

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The retractive forces in drawn low density polyethylene depend on temperature and time. At room temperature, the material looks fairly stable. Above 70 °C, the drawn sample starts to shrink. The shrinkage forces can be observed on a material with fixed ends. At a given temperature, they first increase to a maximum and then drop to a relatively high limiting value. The maximum force and the asymptotic value have a maximum at about 90 °C.

If the sample is heated at a sufficiently slow rate, the restoring force reaches a maximum at about 90 °C and subsequently drops almost to zero near the melting point of the material. The molecular explanation of the observed effects is based on the mobilization of taut tie molecules and on their relaxation at the high temperature of the annealing which permits a pulling of chain sections from the crystal blocks in which the taut tie molecules are fixed. During cooling, the restoring forces are substantially lower than during heating as a consequence of the relaxation of the taut tie molecules by the annealing effect of the previous heating.

Permeation Performance of Polyethylene Used in Containers for Hazardous Materials Transportation
Subtask 16 of Task 12136

J. C. Phillips

The initial phase of this work involved the development of test methods for the permeation performance of polyethylene shipping containers to be used by the Department of Transportation. These experiments consisted of weight loss determinations for an n-alkane series, n-alcohol series, and n-carboxylic ester series. The loss rate, Q_A, results were correlated with an effective carbon atom number, n_e, for each compound. Due to limited chain lengths ($N_A \leq 8$), the shorter members of the alcohol and ester series showed deviations from linear behavior of log Q_A versus N_A.

The final phase of this work was concerned with loss rate measurements at t = 50 °C for permeants of the n-alcohol and n-carboxylic ester series in which chain lengths were extended to $N_A = 16$. For the permeants studied and the polyethylene (PE) bottles used ($\rho \sim 0.92$ g/cm^3 and $\rho \sim 0.94$ g/cm^3), the effective carbon atom number was reasonably correlated with the loss rate (i.e., log Q_A versus n_e was linear and parallel for each density bottle). By using loss rate measurements from the low density bottle for a group of miscellaneous compounds (1,2-dichloroethane, acetone, methyl ethyl ketone, acetonitrile), the loss rate for the high density bottle was adequately predicted for these compounds.

This study has verified, at least for the permeants and PE bottles used, that the effective carbon atom number is a convenient parameter for transferring the results of permeation measurements among shipping containers made from various PE resins and, thereby, simplifies the prediction of transmission performance.

Durability of Paper
Subtask 17 of Task 12136

J. C. Smith, E. E. Toth, E. L. Graminski

Paper used to make currency should have a good balance between durability and cost, as the replacement of worn out currency is an expensive operation. Because of this, the Bureau of Engraving and Printing supports work at NBS to identify and characterize those aspects of the morphology of paper networks which affect durability. The research results are expected to contribute to the development of durable paper made from blended wood pulps instead of the more expensive cotton and linen pulps presently used.

To achieve these objectives, it is necessary to have an improved understanding of the relationship between the structure of paper, the morphology of the fibers, the processing conditions, and the mechanical and physical properties of the paper and its components. Over the past several years, studies at the National Bureau of Standards on the bondability of the pulp fibers and on the cellulose-water interaction in rag and wood pulps have helped to provide some of this background information.

Parameters for characterizing interfiber bond strength can be obtained from tensile tests on a low density open-web handsheet prepared from the pulp to be evaluated. The force-elongation curve from a specimen of this handsheet contains numerous force drops, each drop caused by the breakage of a bond between fibers constituting the handsheet network. The relative number of bonds per unit area can be characterized by the average elongation between bond breaks. The bond strength can be characterized by an average of the force-drop magnitudes, or by an average of the energy losses resulting from the force drops. The average of the force levels obtained in a series of tests can also be used to characterize bond strength. The above parameters, however, are not very precise because of fluctuations in the uniformity of the test specimens.

Recent work has shown that the force elongation curve of a low density open-web test specimen has the form

$$F = A[\exp(x/x_c) - 1],$$

where F is the force, and x is the elongation. The two parameters, A and x_c, are sensitive to the number of fibers per unit area in the specimen tested. Moreover, during a test, A and x_c vary in value as the test proceeds, reflecting damage to the specimen and changes in the location of bond breaks. This possibility of characterizing the state of a specimen at various stages of a test may enable the measurement of bonding parameters with improved precision. Knowledge of the force-elongation curve parameters will also make possible the comparison of bonding parameters obtained from tests on samples of different densities.

Morphologies of the handsheets and constituent pulp fibers are being examined by scanning electron microscopy. Results of these investigations suggest that bonding in currency pulps may be due to the presence of a large fraction of fines which act as a "glue." These fines are not present in the wood pulps, and bonding between wood fibers depends on the ability of their surfaces to conform and establish intimate contacts at the junctions.

During the preparation process, pulp is subjected to mechanical action such as beating or refining. This treatment causes fibers to imbibe water and become more flexible, thereby facilitating interfiber conformation. However, the microstructure of the prepared pulp is influenced by the way in which water is bound to the fibers, and this varies with the kind of pulp material. This is being studied by measuring the proportions of bound and free water in different pulp samples.

The water imbibed by a pulp specimen is measured by solute exclusion. A dextran pulp specimen is added to a solution of dextran in water, and the excess water in the specimen dilutes the solution. The amount of the dilution is measured by polarimetry, and the imbibed water, or fiber saturation point, of the specimen is calculated. Part of the imbibed water is tightly bound to the cellulose and does not freeze at temperatures down to 223 K. This bound water fraction is measured by differential scanning calorimetry.

It is found that beating causes increasing amounts of water to be imbibed by both cotton and wood pulp fibers. However, beating causes an increasing fraction of the water imbibed to be bound in cotton. This does not happen to as great an extent in wood pulp. It is believed that free water promotes flexibility and that bound water is attributed to breakdown of the crystalline structure. Thus, beating of wood pulp produces flexible conformable wood pulp fibers, but causes fibrillation and fines formation in cotton fibers.

MIGRATION AND THE DURABILITY OF POLYMERS IN USE
Task 12138

Polymeric materials now find their principal markets in construction, appliances, transportation, and electrical systems where long-term durability is critical to their competitive performance. Reliable short-term tests are therefore needed for the selection of durable polymers and knowledge of polymer degradation mechanisms is needed to guide the development of protective methods and to improve performance. Technical work this year has emphasized the determination of the mechanism of degradation and stabilization of polyurethanes, the use of thermogravimetric measurements for lifetime prediction, and the development of chemiluminescence methods for the detection of photoinitiated oxidation in polymers.

The most general phenomenon related to the durability of polymers is the effect of protective additives. Almost all commercial plastics have low molecular weight substances incorporated in them to develop or maintain desirable properties. In use, these substances inevitably diffuse through the polymer to some extent and may migrate out of the polymer entirely. The polymer is then left with poorer properties or increased vulnerability to degradation and failure. This is a major failure mode of polymers, and programs concerned with polymer durability must explicitly consider the possiblities of additive migration. A second consequence of migration is that the migrating substance becomes a contaminant of the environment or, in the case of plastic packaging materials, a contaminant of the material being contained. This raises questions about the toxicological consequences of such migration. Contamination of food from food packaging materials is regulated by the Federal Government through the Food and Drug Adminstration, and the control of migrating substances presents an enormous challenge to the scientific basis of regulations.

The number of commercially usable polymer-additive combinations is too large to be considered efficiently on a case by case basis, either for selection of materials of optimum durability or for regulation of food and environmental contamination. General material models capable of predicting migration under a variety of service conditions are needed to organize polymer-additive combinations into classes for consideration. The development of these material models is the overall objective of work done in this task.

Technical activities on additive migration that contribute to this task include (1) the experimental measurement of additive migration by several methods, (2) the compilation of critically evaluated data from this laboratory and the literature, (3) mathematical modeling and empirical correlation of diffusion data for analysis of data and rapid estimation of migration, and (4) fundamental theoretical studies of polymer behavior that can provide truly general predictive models.

Hydrolytic Degradation of Polyester Polyurethane Elastomers
Subtask 1 of Task 12138

D. W. Brown, R. E. Lowry, L. E. Smith

Polyester based polyurethanes degrade in moist air because of the acid catalyzed hydrolysis of the ester linkages [1]. With soluble polymers, acid content, A, and number average molecular weight, M, vary with time, t, according to [2]:

$$A = A_0\, e^{kt} \text{ and } M^{-1} = M_0^{-1} + A_0(e^{kt} - 1)$$

Here the subscripts indicate initial values, and k is the fractional rate of increase in acid content.

These findings were applied to the study of insoluble urethane foams used in the fuel cells of military aircraft [3]. Foam samples were aged until soluble. Subsequent agings then enabled us to calculate k, which permitted prediction of the remaining foam life. A test using swelling in dimethylformamide was developed that permits one to judge very quickly the condition of foam in existing installations.

Polyester polyurethanes are sometimes stabilized against hydrolysis by the incorporation of carbodiimides [4]. These compounds destroy acid by the reaction:

$$\text{-N=C=N-} + \text{-CO}_2\text{H} \xrightarrow{k'} \text{-}\underset{\text{H}}{\underset{|}{\text{N}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\underset{\text{O=C-}}{\underset{|}{\text{N}}}\text{-} \qquad (1)$$

We have measured k' for reaction of a mono- and of a polycarbodiimide in polyesterdiols, in a polyester polyurethane, and in tetrahydrofuran solutions of a polyester-diol [4]. Except for the reaction of the polycarbodiimide in the polyurethane, the kinetics of reaction [1] were second order overall. Values of k' cover a relatively small range considering the enormous range of bulk viscosities.

Attempts were made to predict the behavior of polyesters undergoing wet aging using only k and k'. The predicted stabilization is much greater than observed. Reasonably good prediction can be made if a third reaction, one for disappearance of carbodiimide by a zero order process, is introduced into the mechanism. This reaction could be due to uncatalyzed hydrolysis or to hydrolysis catalyzed by a material not reactive with carbodiimide; present evidence favors the latter hypothesis. If confirmed, better stabilization might be achieved by destroying this catalyst. Work in this area is continuing.

Polyester polyurethanes containing carbodiimides have been aged for periods approaching one year at temperatures of 85, 55, and 35 °C at 100 percent relative humidity. Acid content, molecular weight, and carbodiimide content are all being followed. At 85 °C, lifetimes of polyester polyurethanes with three weight percent carbodiimide are about threefold longer than those of unprotected samples. For unknown reasons, the same carbodiimide content in polyesters gives tenfold greater lifetimes. This study is also being continued.

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Thermogravimetry Studies of Polymer Degradation
Subtask 2 of Task 12138

B. Dickens

Thermogravimetry is important because several of the constant heating rate and isothermal techniques are easy to apply, because excellent commercial apparatus is readily available, and because it can be used to study any condensed phase, soluble or insoluble.

The scientific literature contains many articles on the determination of the kinetic parameters of polymer degradation using thermogravimetry, but there is little or no agreement between the published values of the parameters. Various estimates differ by as much as 100 percent. Therefore, we are currently investigating the nature of the rate-determining weight-loss process and the use of thermogravimetry to provide realistic estimates of meaningful kinetic parameters involved in the thermal degradation of polymers.

To this end, the technique of factor-jump thermogravimetry was developed in our laboratory and has been used to study the degradation of several vinyl polymers in vacuum and in nitrogen. The apparatus is more highly automated and more flexible than commercially available apparatus. The technique has several distinct advantages:

(1) it is able to determine activation energy using only one sample so that problems arising from differing thermal histories of two or more samples are avoided,

(2) several activation energies are determined in each experimental run so that changes in sample behavior can be discerned,

(3) because the activation energies are determined from locally extrapolated rates, no knowledge of the initial and final sample weights is necessary, and

(4) automatic feedback adjusts the experimental conditions for changing sample behavior. Points 3 and 4 allow the method to treat multi-stage degradations successfully.

The results of thermogravimetric experiments conducted on several polymers under vacuum conditions were fairly erratic and difficult to interpret. Although it is generally difficult to determine whether the instability results from the apparatus or the method, it has now been shown convincingly that a large part of the variation is in the thermal history of the sample. Only in the cases of polymers degrading with very long zip lengths to produce mainly monomer could results of chemical rather than physical significance be obtained in vacuum. The most fiducial results for all polymers studied so far have been in slowly flowing N_2, but even there the experimental conditions play a surprisingly large role. For isotactic polypropylene, the apparent activation energy for thermal degradation in vacuum was determined to be 61.5 ± 0.8 kcal/mole; for linear polyethylene it was 65.4 ± 0.5 kcal/mole. In slowly flowing N_2, the apparent activation energy is 54 ± 1 kcal/mole for isotactic polypropylene and 51.5 ± 0.5 kcal/mole for atactic polypropylene. For linear polyethylene, the value is 61 ± 1 kcal/mole. These values are significantly different from the vacuum values and from most of the published values. In the case of polypropylene, a reasonably careful study carried out elsewhere assigns 56 ± 5 kcal/mole to atactic polypropylene and 51 ± 5 kcal/mole to isotactic polypropylene. Those results are 5-10 times more imprecise than the results from factor-jump thermogravimetry. We will continue to use the factor-jump thermogravimetry technique to study the effects of experimental conditions, molecular weight, and branching on the activation energy of thermal degradation of polypropylene, polyethylene, and several other polymers.

Computer programs have been written to drive the apparatus and to conduct various statistical tests to provide estimates of the precision of the results and to reduce as much as is feasible the effect of aberrant values. These programs and procedures have been documented in a User's Guide.

Variable Heating Rate Thermogravimetry
Subtask 3 of Task 12138

J. H. Flynn

The prediction of the lifetime of a polymer by extrapolation from weight-loss data requires a thorough analysis of the degradation kinetics over a wide temperature range. Techniques have been developed in which entire kinetic spectra are compared among experiments performed at heating rates from 6 deg/min to 9 deg/day. Simple methods of plotting data from these techniques have been used for diagnosing shifts in reaction mechanism, uncoupling of competing processes, and testing the validity of kinetic models.

Weight-loss studies are continuing on polystyrene, poly(methyl methacrylate), and polyurethanes in vacuum and in atmospheres containing nitrogen, air, and water vapor. Subtle changes in mechanism have been exposed for several of these cases under the milder conditions of the above techniques. It now appears that rapid conventional thermogravimetric techniques at high temperatures are inappropriate for the prediction of service lifetime of these polymers.

<u>Chemiluminescence From Oxidizing Polymers</u>
Subtask 4 of Task 12138

R. E. Florin, B. Dickens

Polymers emit light weakly during oxidation. This effect has aroused recent interest as a means of monitoring oxidative deterioration of polymers. A widely accepted theory of the effect is that the light is emitted during the termination step of the oxidation chain reaction. Although the quantum yield of light emission is estimated to be only one photon per 10^9 terminations, this inefficiency can be overcome by the technqiue of counting individual photons, which leads to an extremely sensitive method, potentially capable of detecting oxidation at temperatures only a little above those of normal service. In contrast, more accelerated aging methods require a long extrapolation from high test temperatures to service temperatures, and the mechanism of degradation probably changes.

The general objective is to obtain a representative data base for correlating chemiluminescence emission rates with overall oxidation rates for polymers of differing physical and chemical characteristics. The appropriate kinetic parameters are the rates of initiation, propagation, and termination. We have devised a method for measuring one of the individual rate constants of the process, that of termination. A prototype photon counting apparatus has been constructed. Ultraviolet light activates a photoinitiator solute which then attacks the solvent which may be polymer, rubber, or liquid. The light can be cut off suddenly, and decay in the oxidation rate followed to give estimates of the rate constants of the termination reaction. Oxidations initiated thermally, without irradiation by light, give estimates of the rate of initiation of polymer oxidation itself, i.e., the rate of transfer from the initiator to the polymer. This is because under these conditions the polymer oxidation is a chain reaction operating in the steady state, and the rate of initiation is equal to the rate of termination.

Evaluation of transfer of radicals from the photo-initiator to the polymer provides essential information on the dispersion of the initiator in the polymer and also allows us to study the influence of the "cage effect" on the initiation process. Evaluation of the termination rate constant under various conditions allows us to study the influence of the cage effect on the termination process. One example of the cage effect is when two radicals, newly produced adjacent to one another by a bond-breaking process, are held in close proximity to each other by the matrix and react with one another without attacking their environment.

If a radical escapes from the cage, it continues the polymer oxidation process until it reacts with either another similar radical or an added radical-trapping molecule. Effects of cages bring severe complications in the understanding of oxidation and are poorly characterized.

The chemiluminescence will also be used to study initiation by sensitive groups on the polymer, such as the ROOH groups produced during oxidation under normal conditions. Other parameters needed to complete the characterization of the oxidative chain reaction are the kinetic chain length and the total amount of oxidation. These can, in principle, be determined with techniques already described in the literature. However, to achieve sensitivity useful at the low levels of oxidation at which the chemiluminescence photon counting method gives useful information, these literature techniques will need further development.

The extreme sensitivity and very low levels of light emission bring their own problems. Extreme care was necessary to produce a sample enclosure with a level of luminescence low enough for the sample to be "seen." There are problems in dissolving enough photoinitiator in polymers without precipitating it as a second phase. Also, careful measurements have shown that oxidation phenomena are not as simple as they are usually thought to be.

The procedure described here is now highly automated, the apparatus being controlled by a laboratory computer. The existence of spikes of high counts (cause unknown) and of zero or very low counts from occasional non-opening of the shutters required the writing of a trimmed-mean estimating program. Other programs provide needed processing of data and continuously update the level of photoinitiator left in the sample.

Currently, the optimum technique is being developed, and calibrating runs are being carried out on simple organic compounds for which the termination rate constants are known. The procedure and programs developed up to now are being documented in a User's Guide.

Migration of Oligomers and Antioxidants From Polyolefins
Subtask 5 of Task 12138

S. S. Chang, W. J. Pummer, J. R. Maurey, L. E. Smith

During the last two years, a rather thorough experimental investigation of the kinetic behavior of the migration of oligomers and antioxidants from polyolefins into food and food-simulating solvents has been carried out. This program is under the sponsorship from the Food and Drug Administration (FDA). Extractions of migrants by actual foods are being carried out by a separate FDA contract at Arthur D. Little, Inc. The only food used in the program here is the corn oil, for the purpose of finding some solvents that simulate the extracting action of food oils.

A large number of experimental variables have been investigated. These variables are (1) polymers--linear polyethylene, branched polyethylene, and isotactic polypropylene; (2) migrants--n-$C_{18}H_{38}$, n-$C_{32}H_{66}$, and BHT;

(3) solvents--corn oil, tributyrin, trioctanoin, ethanol, ethanol-water mixtures, water, n-heptane, and n-octadecane; (4) temperature--30 and 60 °C. Furthermore, the initial concentrations of the migrants in the polymers and the thickness of the sample plaques have also been varied. Besides the kinetic studies, equilibrium properties such as solubilities and partition coefficients have also been studied. The migrants used are labeled with radioactive ^{14}C, to yield a detectibility of 10^{-10} g if needed. The extraction experiments generally require a few weeks to a few months to complete; however, some experiments are completed within a few days, while some may last longer than a year.

There are about two hundred extraction experiments scheduled. Most of these experiments are now completed. The diffusion coefficients observed vary from near $10^{-6}cm^2s^{-1}$ to less than $10^{-15}cm^2s^{-1}$. Some of the experiments indicate an ideal Fickian behavior, especially for pre-swollen polymer in one extreme and for non-swelling solvents in the other extreme. For the intermediate cases, the diffusion coefficient may increase from an initial value and then level off at a higher value or may increase drastically, such that the migrant is exhausted before seeing the leveling off of the diffusion coefficient at a higher value.

From these results, certain generalizations and correlations can be drawn for the migration of oligomers and antioxidants from polyolefins. These findings may form a basis for the estimation or prediction of the diffusion coefficients in situations not mentioned above.

If all other parameters are held constant, then it seems that the ranking of importance for the parameters on the diffusion coefficient of migrants from polyolefin is as follows: solvent, temperature, additive-type, polymer type, additive concentration. The first three parameters are far more important than the remaining two. There are overlapping cases of the ranking at the extremes of these parameters.

Effect of Solvent: Solvent is the single most important parameter in the correlation scheme. For moderate solubilities, e.g., above one percent, one may make correlation of the diffusion coefficients only to the solvents irrespective of other variables such as polymers, additives, additive concentrations, and temperatures. Figure 1 shows the correlations of diffusion coefficients in several solvents versus that in ethanol, while other variables are kept identical. Although by changing solvents the diffusion coefficients may change by a factor of more than 2000, the simple correlations indicated in figure 1 can reduce the variation down to a factor of 3 or less. The two correlations shown are for n-heptane, and for the combination of corn oil, tributyrin, and trioctanoin.

The diffusion coefficients in corn oil, tributyrin, and trioctanoin are nearly identical to that in ethanol within a factor of three. The ratios of diffusion coefficients among the two pure triglycerides and the corn oil are in general less than 1.5. Therefore, either ethanol, tributyrin, or trioctanoin can be used to simulate the extractive action of corn oil in a great variety of conditions involving different additives, polyolefins, and temperatures.

The accelerated action of n-heptane over that of the corn oil or its equivalents is clearly demonstrated in Figure 1. The diffusion coefficient is only 10 to 20 times higher in the case of high diffusion coefficients, such as in the case of highly loaded n-$C_{18}H_{38}$ in branched polyethylene at 60 °C. However, the disparity increases as the diffusion coefficient is decreased, as may be seen in other correlations with temperature, etc. Thus, for the case of extracting higher molecular weight oligomers, n-$C_{32}H_{66}$, from linear polyethylene at 30 °C, the diffusion coefficient in n-heptane is about 1000 times higher than that in corn oil or its equivalents.

Combining the effects of the accelerating action and the greater solubility of n-heptane over that of ethanol for polyolefin oligomers, the extract of the whole polymer by n-heptane contains a large amount of higher molecular weight oligomers that may be barely present or absent in the ethanol extract under the same conditions.

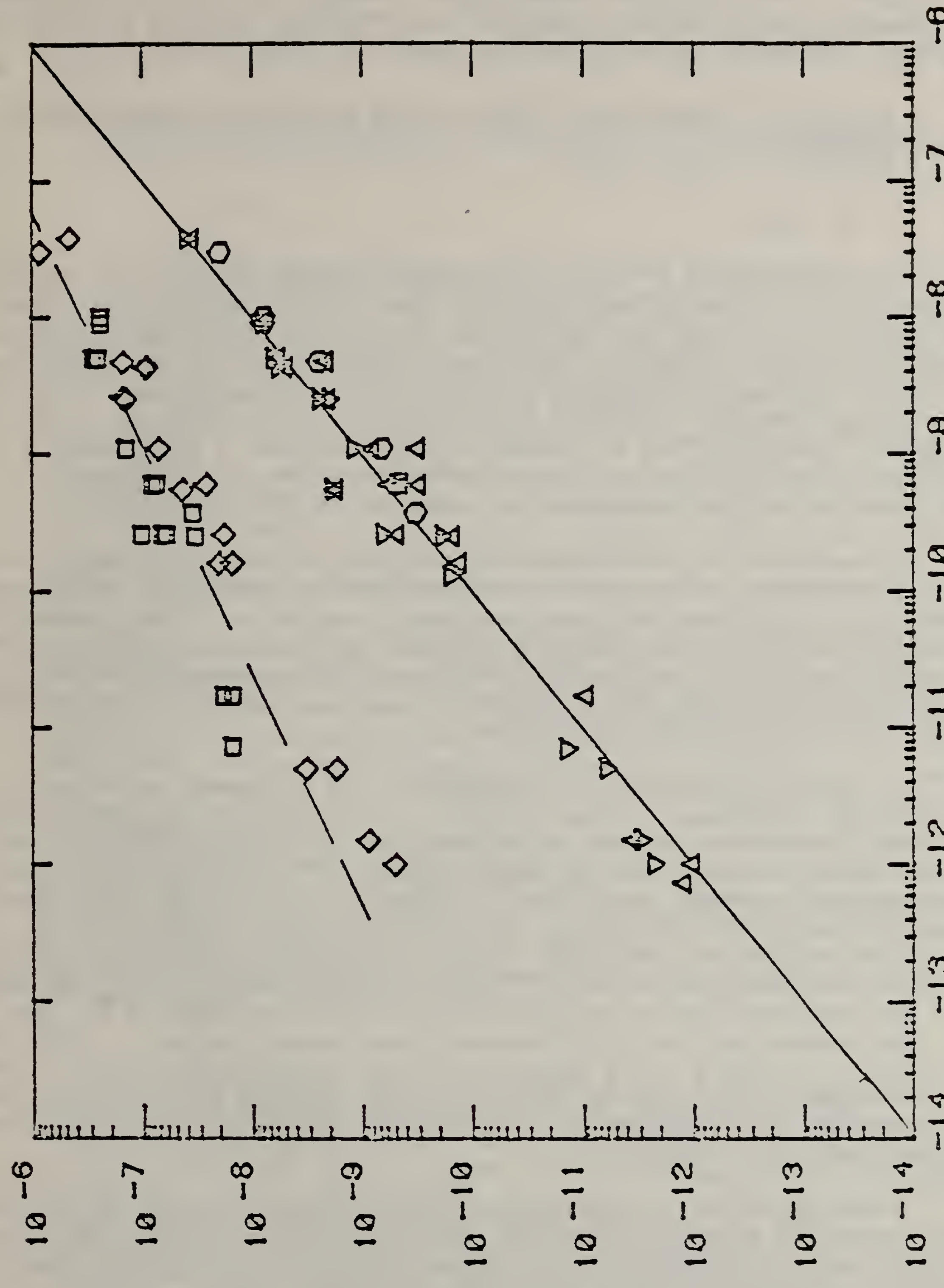
When the solubility is low, e.g., in the cases of using ethanol-water mixtures or water as solvents, it is difficult to make simple correlations as a function of solvent without taking other variables, such as polymers, additives, partition coefficients, and temperatures, into account.

Effect of Temperature: Similarly, diffusion coefficients for additive migration at 30 °C may be correlated to the diffusion coefficients at 60 °C by a single relationship to a factor within 5, irrespective of all other variables. Again, the effect is minimized at higher diffusion coefficients and increased at lower diffusion coefficients. Better correlations can be made by separating other variables such as additives and polymers. The activation energies observed range from 20 $kJmol^{-1}$ to 200 $kJmol^{-1}$.

Effect of Additive: Changing of additives while keeping all other variables the same also changes the diffusion coefficients drastically. It is not possible to construct a simple correlation with respect only to the additives but irrespective of all other variables. Reasonable correlations may be made for additive-polymer combinations. Even then, definitive structures in the correlations due to solvent or temperature are observed.

Effect of Polymer: For all cases studied, the diffusion coefficient changes, at maximum, by a factor of less than 50 due to the changes from low crystallinity branched polyethylene to high crystallinity linear polyethylene and isotactic polypropylene. Fine correlation requires other variables such as additive and temperature to be kept constant.

Effect of Additive Concentration: If the additive, such as BHT, is insoluble in the polymer or does not act as a plasticizer, no significant effect on diffusion coefficients due to the change in additive concentration has been observed. Changing the concentration of n-$C_{18}H_{38}$ from one percent to 0.01 or ten percent may produce a change in the diffusion coefficient by a factor of 40 in the cases studied. Correlations as a function of concentration for a particular additive but irrespective of other variables are possible.


D(ETCH), cm2/s

Conclusion: From the above observations, one can make a reasonable order of magnitude estimate of the diffusion coefficient if any of the variables such as solvent, temperature, polymer, and additive concentration is changed, while the estimation of the effect of changing of additives without specifying other conditions would be rather difficult.

A Critical Compilation of Data on the Diffusion of Additives in Polymers
Subtask 6 of Task 12138

J. H. Flynn

The compilation of kinetic constants for the diffusion of organic compounds in polymeric materials will result in a reliable data base which may be utilized both to evolve theoretical models for diffusion mechanisms and to establish empirical relationships for the prediction of the migration of chemicals and additives in polymers used in the food packaging, chemical container, and transportation industries. With support from the Office of Standard Reference Data, a comprehensive collection of kinetic data on the diffusion of organic compounds in polyolefins has been completed and prepared for publication.

The tables for low density polyethylene, high density polyethylene, polyisobutylene, polypropylene, hydrogenated polybutadiene, poly(4-methylpentene-1), ethylene-propylene copolymers, and self-diffusion of polyolefins contain over 250 polymer-migrant entries. Diffusion constants at temperatures from -30 to 190 °C, activation energies and preexponential factors for the diffusion process and parameters for the concentration dependence of the diffusion constant are included.

A special feature of this compilation is an extensive section of annotated references. These include: (1) as complete a characterization of each polymer and migrant as is possible, (2) a description of the experimental methods used to determine the diffusion constants, and (3) the assumptions made, equations utilized, and calculations performed to obtain the data in the tables. The justification for this lengthy section is twofold. The large effects of structure and conditioning of the polymer substrate on the diffusion process require a detailed description of the characterization and pretreatment of the polymers if the data are to be compared and their differences interpreted. Secondly, since diffusion constants are a function of time, concentration, and distance, a knowledge of the experimental conditions, methods of measurement, and theoretical models evoked for the calculations are also essential for an understanding of the data.

The tables exhibit remarkable consistencies, considering the great variations in diffusion constants which can be brought about by thermal, mechanical, and solvent action. These consistencies lend hope that useful correlations may be developed from these data.

Work has begun on a similar compilation of kinetic data for the diffusion of organic migrants in polystyrene--a polymer of commercial and theoretical importance--which in contradistinction to the polyolefins, is in a physical state below its glass transition temperature at normal service temperatures where most of the diffusion data on it have been obtained.

Measurement of Migration in Polymers by Inverse Gas Chromatography
Subtask 7 of Task 12138

G. A. Senich

Inverse gas chromatography (IGC) is being evaluated as a method for studying the thermodynamic and kinetic interactions of volatile compounds or probes with polymers. The experimental procedure is similar to conventional gas chromatography with the exception that a solid or molten polymer replaces the usual liquid stationary phase. Low carrier gas flow rates insure that the probe retention time is sufficiently long for a steady-state distribution between the vapor and polymer phases to be established. The specific retention volume V_g^o, a measure of the thermodynamic interaction between the probe and polymer, is then determined from the total amount of carrier gas necessary to elute the probe from the column. Experiments with alkanes and well characterized NBS polyethylene samples have been performed both above and below the polymer melting temperature. The V_g^o values determined above the melting temperature agree with results in the literature derived for similar systems. An error analysis has been effected to establish the precision which can be expected for such experiments. Since the amorphous fraction is the sole contributor to bulk sorption of the probe molecules below the melting temperature, the accuracy to which the percent crystallinity is known limits the reliability of determinations in this temperature region. The polymer-probe interaction parameter has been calculated from V_g^o by applying relations derived from the equation of state based polymer solution theories of Flory and of Sanchez and Lacombe, both yielding similar results. This parameter can be used to predict a limiting value of the partition coefficient, which describes the distribution of the probe between a polymer and a non-swelling liquid in contact with it, provided that the solubility of the probe in the liquid is known to be small.

The migration kinetics of a probe in the polymer phase can be related to the degree of broadening of the eluted probe pulse over its initial injection distribution. At high carrier gas flow rates, there is insufficient time for the probe to reach a steady-state distribution between vapor and polymer phases. The degree of peak spreading is related to the rate of mass transfer occurring in the column, provided that contributing instrumental factors, such as dead volume, are negligible. The magnitudes of various gas phase mass transfer processes have been estimated and their effects minimized in a series of studies on diffusion of octadecane in polyethylene. The diffusion coefficient has been determined for this system and found to be extremely sensitive to the geometry of the polymer film present on the spherical support particles. Knowledge of the film thickness distribution, in addition to its average value, is critical to the experimental determination of reliable diffusion coefficients by IGC. Future work will include studies of diffusion in polymer systems with clearly defined geometry. IGC experiments on diffusive processes in glassy polymers will also begin.

Diffusion Coefficient of Medium Size Molecules in Semicrystalline Polymers
Subtask 8 of Task 12138

A. Peterlin, F. L. McCrackin

An empirical correlation of the diffusion coefficient of a number of molecules with sizes between N_2 and SF_6 in natural rubber and in polyethylenes of increasing crystallinity can be given by

$$D' = KD^m$$

where K and m depend on the polymer but not on the penetrant. The diffusion coefficients are given by this expression within a relative error of 4.7 percent. This expression may be interpreted in terms of the fractional free volume, f, concept of the material transport. According to this model, the diffusion coefficient is given by

$$D = A \exp(-B/f)$$

where B depends on the size and shape of the penetrant molecule while f and, to some extent A, depend exclusively on the polymer. By introducing this expression for D and D', one obtains m = f/f', which permits the calculation of the ratio of the fractional free volume in the polymers investigated. For the cases investigated, f of the amorphous component, which is responsible for practically all the material transport, depends substantially on the crystallinity. At the highest observed crystallinity of 0.77, the fractional free volume seems to be only 67 percent of the fractional free volume in polymer with the low crystallinity of 0.29. The situation is still more extreme if one includes natural rubber which does not contain any crystals. Polyethylenes with crystallinity 0.77, 0.43, and 0.29 have a fractional free volume which is 0.58, 0.76, and 0.86, respectively, of the fractional free volume of the purely amorphous natural rubber.

Measurement of Antioxidant Migration by Fluorimetry
Subtask 9 of Task 12138

F. W. Wang

The migration of antioxidants from polymer films is being studied by extraction experiments. In an extraction experiment, a plane sheet of polymer with uniform concentration of an antioxidant is immersed in a limited amount of well-stirred solvent. Then, the amount of the antioxidant extracted by the solvent is determined at various times by fluorimetry.

Experiments were performed to measure the extraction on N,N'-diphenyl-p-phenylene-diamine (DPPD) by heptane at 22.0 °C from 0.27 mm thick low-density polyethylene films containing 8.4 x 10^{-3} percent DPPD. The results showed that all the DPPD had been extracted out of the films within four hours and that the plots of the weight of DPPD extracted against the square root of time were sigmoidal and non-Fickian. These results and others to be collected will be compared with the predictions of a theory being developed by Dr. F. L. McCrackin.

Excimer Fluorescence Technique for the Study of Polymer-Segment Mobility
Subtask 10 of Task 12138

F. W. Wang, R. E. Lowry

The study of polymer-segment mobility is of practical as well as scientific interest. Such a study will on the one hand contribute to the design of polymeric reagents and on the other hand, shed some light on "internal viscosity," an idea introduced by Kuhn some 35 years ago and yet still argued about [1,2]. Therefore, we initiated a program to measure polymer-segment mobility by a novel technique based on excimer fluorescence.

An excimer is formed by the association of an excited molecule with another molecule in its ground state. Such an excimer is characterized by a broad structureless fluorescence which is shifted to longer wavelengths with respect to the fluorescence spectrum of the isolated molecule. Similarly, excimer formation may take place by intramolecular processes in polymers carrying excimer-forming groups. Thus, excimer fluorescence has been observed in dilute solutions of polymers such as polystyrene, polyvinylnaphthalene, and poly(1-naphthyl methacrylate).

We synthesized a random copolymer of methyl methacrylate and 1-pyrenylmethyl methacrylate as well as a random copolymer of methyl acrylate and 1-pyrenylmethyl acrylate, the mole fractions of pyrene-labeled monomers being 0.05 and 0.03, respectively. We then measured the fluorescence spectra for dilute degassed solutions of these polymers at 22.0 °C in ethyl acetate and in mixtures of ethyl acetate and glycerol tripropionate, which have the same chemical nature but different viscosity.

For a given polymer, the value of I_D/I_M, the ratio of the fluorescence flux emitted by pyrenyl excimers to that by isolated pyrenyl groups, depends on polymer conformation as well as the rate constant k_a for the diffusion-controlled association of an excited pyrenyl group and a ground-state pyrenyl group to form a pyrenyl excimer. However, by using mixtures of solvents of the same chemical nature but different visocisty, we were able to study the effects of solvent viscosity on I_D/I_M without modifying the polymer conformation to any significant extent. Thus, at the low enough temperature of our investigation, the ratio I_D/I_M at photostationary conditions was proportional to k_a [3]. Since k_a in turn depends on the polymer-segment mobility, measurements of I_D/I_M as a function of solvent viscosity allowed us to determine the effects of solvent viscosity on the polymer-segment mobility.

We found that the experimental curves of the reciprocal of I_D/I_M (or equivalently the reciprocal of k_a) against the solvent viscosity were concave downward. This finding agrees with Cerf's proposal [4] that the highly diversified segmental motions of linear polymer chains belong mainly to two classes which follow diffusional and non-diffusional behavior, respectfully, and which may coexist, the former having the reciprocal of the characteristic rate constant proportional to the solvent viscosity and the latter having the reciprocal of the characteristic rate constant a linear function in the solvent viscosity with a non-zero constant attributed to "internal viscosity."

Additional experiments will be performed to study the variation of polymer-segment mobility with polymer structure, solvation of polymer, and polymer-polymer stereocomplex association.

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Assessment of Transport Mechanisms for Radon in and Through Building Materials
Subtask 11 of Task 12138

R. J. Rubin

Accumulation of radioactive radon gas in buildings poses a health hazard. High levels of radon are encountered in certain "hot" geological areas where it emanates naturally from the ground. Certain building materials, such as gypsum board, also contain higher than average amounts of radon. Under an interagency agreement with the EPA, NBS has very recently undertaken the task of studying radon transport in building materials. It involves a cooperative effort between three NBS Centers: Radiation Research, Building Technology, and Materials Science. The initial phase of this project is to critically assess the current state of knowledge of radon transport through or emanation from building materials. The Polymer Science and Standards Division's role is to assess current transport mechanisms and models.

DIELECTRIC PLASTICS DESIGN AND PERFORMANCE
Task 12139

Trends in dielectric application of polymers include use of higher working voltages in electrical apparatus and transmission lines to conserve materials, save space, and reduce weight. This work provides manufacturers (polymer manufacturers, film fabricators, transducer manufacturers), trade associations (EPRI), and Government agencies (DOE, DOD) with data, measurement methods, and concepts which identify limitations in polymer performance traceable to manufacturing practices. For example, steam curing of extruded polyethylene insulated cables results in lifetime limiting voids and inclusions. With a trend toward increased use of underground transmission of electric power, improved insulation performance is required. Data and recommendations from this work go directly to cable manufacturers and funding organizations (i.e., EPRI, DOE) who are able to specify and require manufacturing changes leading to improved products.

Other trends are new, rapidly growing applications of polarized polymers as pyro- and piezoelectric transducers. Transducer manufacturers as well as private and Government transducer users (DOD, EPA, HHS) need reliable information connecting polymer structure and polymer performance to the design of improved transducers. This work will help transducer material and device manufacturers design and develop commercial polymer transducers for use in health and safety applications (pulse monitors, therapeutic and diagnostic sound measurements, auto crash sensors, prosthetic fitting devices, nontoxic antifouling coatings, mine disaster warning devices) and in the areas of national security (microphones, hydrophones, intrusion detectors, ultrasonic and infrared imaging devices, fusing devices, etc.). Important scientific opportunities of this work include breakthroughs in understanding the basic factors in electrical failure of polymers and discovery of novel measurement methods which are becoming possible with newly developed polymers. For example, this work attempts to show how polymers interact with electronic and ionic charges and how structure can be modified to optimize piezoelectric and semiconducting properties.

Polymer Insulation for Superconducting AC Power Transmission Cables
Subtask 1 of Task 12139

F. A. Khoury, F. I. Mopsik, S. J. Kryder, L. H. Bolz

This project, sponsored by and carried out in collaboration with Brookhaven National Laboratory (BNL) with DOE funds, is part of a program for evaluating the suitability of various types of polymer films for use (in tape form) as the electrical insulation in high power superconducting a.c. transmission cables operated at 6-8 K. Such cables, in which the superconductor is Nb_3Sn, are currently under development at BNL. Among the guidelines used for selecting the insulation for such cables is that the dielectric constant (ε) should be 2.5 or less and that the dielectric loss ($\tan \delta$) should preferably not exceed 20×10^{-6} at the cable operating temperature range and 60 Hz.

This subtask is primarily concerned with the measurement of the dielectric properties (ε, tan δ) of polymer films at cryogenic temperatures. These measurements, for which NBS has a unique instrumental facility, are coupled with studies of aspects of the fine structure of the films in an effort to determine the influence of various structural parameters (e.g., crystallinity, molecular orientation, voids) on the dielectric properties of the films. In addition to determining whether specific types of commercially available films meet the established criteria for dielectric properties, these studies are aimed at providing data relevant to the design and production of films exhibiting optimum dielectric properties for the intended end use. In a less extensive effort, the compressibility of the polymer films is measured. This latter feature is relevant to the determination of the optimum conditions (e.g., tape tension) necessary for winding the films (sliced into tapes) around the cable core, so as to yield a cable exhibiting appropriate flexibility for winding onto storage drums 10 feet in diameter.

In FY80, this project was mainly concerned with studying laminates made from two layers of a new, ~ 50 μm thick polypropylene bound together by a polyurethane layer. Measurements made last year indicated that these laminates had substantially lower loss than ones made from older, thinner (25 μm) polypropylenes and could meet the requirement that tan δ not exceed 20×10^{-6} at 6-8 K, which the older ones could not.

Dielectric loss studies were made on two series of laminates. The two series had different yellow dye concentrations (0.7 percent and one percent) in order to see if the presence of dye affected the dielectric loss. The dye is added for visual monitoring of tapes made from the laminates as they are wound to form the cable insulation. In both cases, tan δ was $12\text{-}15 \times 10^{-6}$ at 6-8 K, indicating that the added dye did not affect the loss and that the loss criterion could be met.

Another series of measurements was made on laminates of nominal 80, 100, and 120 μm thickness from polypropylenes of 40 and 60 μm thickness. In addition, the 60 μm polypropylene film was measured separately. These graded thicknesses for the laminates will be used in a cable made for voltage testing to better distribute the voltage stresses across the insulation. The results showed that the loss at 6-8 K decreased with increasing thickness showing that the polyurethane layer, which had a constant thickness in all the laminates, contributed significantly to the loss. The values for tan δ were $18\text{-}20 \times 10^{-6}$ for the 80 μm laminate and $10\text{-}12 \times 10^{-6}$ for the 120 μm laminate. The loss for the polypropylene alone was $6\text{-}7 \times 10^{-6}$, one of the lowest values seen for any polypropylene. These data were then combined to show that the suitably low loss of the present laminate as compared to the older, less satisfactory, laminates was due both to the intrinsically lower loss of the polypropylene itself and to the reduction in the amount of polyurethane present, since only one bonding layer was needed.

In other dielectric measurements, an epoxy composite that was intended for use in bushings was measured for dielectric loss.

All the laminates measured dielectrically were also measured for compressibility when stacked in layers. These data are necessary for predicting cable bendability. The series of graded laminates was also examined microscopically. There was a considerable reduction in void content in the polyurethane layer compared to earlier laminates. This indicates better control over the laminating process and a reduction in possible breakdown problems under voltage stress.

Successful improvement of these materials is traceable in large part to the measurements and analysis from this work which is fed back to the manufacturers to guide processing changes.

Polymer Tape Insulation for Oil Impregnated AC Power Transmission Cables
Subtask 2 of Task 12139

F. A. Khoury, F. I. Mopsik, S. J. Kryder, L. H. Bolz

Oil impregnated paper (cellulose) tape has been, for many years, one of the most commonly used types of electric insulation in high power ac transmission cables. The current and projected needs for more efficient power transmission systems have elicited considerable interest in the development of oil impregnated or oil filled cables operated at 700-1000 KV, in which polymer tape insulation will be used instead of the conventional paper tape which is unsuitable because of its large dielectric loss.

In a project sponsored by Brookhaven National Laboratory with DOE funds, a program has been initiated in the Polymer Science and Standards Division for evaluating the suitability of various types of impregnated ac transmission cables. The goals of this study are: (a) the measurement of the dielectric constant and dielectric loss of candidate films between 273 K and 423 K; (b) the determination of the dependence of the dielectric loss on the fine structural characterisitics of the films; and (c) the specification of the dielectrically most suitable type of film for the intended end use.

The dielectric measurements carried out this past year have focused on a series of drawn polyethylene tapes prepared for Brookhaven by Battelle Institute. Three different base polymers were used under two different rolling conditions. The conditions were a roll temperature of 298/303 K with a thickness reduction ratio of 5-7, and a roll temperature of 348 K with a thickness reduction ratio of 8.3. All the samples were measured under standard temperature cycling to check the effects of thermal cycling.

The three different polyethylenes showed quite different loss characteristics. One of them exhibited a low level of loss (tan δ less than 30×10^{-6}) that did not change much on thermal cycling. The other two had an initial tan δ at 303 K of 80×10^{-6} and 50×10^{-6} all at 100 Hz. The latter two showed substantial reductions in loss at 303 K with thermal cycling to 353 K, 373 K, and 383 K in three successive sets of measurements. All the specimens showed substantial changes in dimensions as reflected in the measured capacitance. The reason for these loss differences as well as the changes in loss with thermal cycling is unknown. One possibility may be differences in the raw polymer (cleanliness and additive content). There were some hints that relatively volatile materials did contribute to the loss. No correlation was found with sample density.

The density, wide angle x-ray diffraction, and small angle x-ray diffraction of the samples were measured both before and after thermal cycling. The most notable effects were found in the density. The tapes rolled at 298/303 K had an increase in density corresponding to an increase in crystallinity from ∿ 66 percent to ∿ 75 percent, while those rolled at 348 K had an increase of crystallinity of ∿ 72 percent to ∿ 77 percent. Some samples of one of the tapes rolled at 298/303 K were thermally cycled as in the dielectric measurements and forwarded to Brookhaven for measurement of thermal conductivity changes induced by the thermal cycling. These data are important for predicting the dissipation of heat generated during power transmission.

The results summarized above, coupled with earlier measurements on the effect of thermal cycling on the dielectric properties of the experimental polyethylene tapes made by Battelle Institute, have emphasized the need for modifying processing conditions in order to produce tapes which are dimensionally and dielectrically stable to thermal treatments in the range 273-383 K. It is expected that the normal operating temperature of the cables will be 355-365 K.

Structure and Performance of Piezoelectric Polymers
Subtask 3 of Task 12139

G. T. Davis, M. G. Broadhurst

The objectives of this task are to study the molecular motions, structural changes, and electrical properties associated with the process whereby polymers are made piezoelectric. Information gained from these studies will be used to optimize piezoelectric and pyroelectric response with respect to both initial activity and long-term stability.

While piezoelectric and pyroelectric activity from polymers is comparable to that from good ceramic materials, other properties of polymers often make them the preferred transducer material. Some of the polymer properties which make them so useful include toughness, flexibility, low density, broad band response, close acoustic impedance match to water, and ease of fabrication. The interest in the use of polymeric transducers continues to increase as evidenced by the requests from other Government agencies, by the large number of requests for information by mail, phone, and personal visits, and by the 20 papers presented at the American Physical Society meeting in March 1980.

During the past year, considerable effort was expended in the preparation and characterization of gamma phase PVDF in order to investigate its poling characteristics. A surfactant, siloxane-oxyalkylene block copolymer (L-520) produced by Union Carbide was deposited from ethanol solution onto PVDF powder so as to comprise two weight percent additive. The alpha phase which forms upon cooling from the melt is transformed to gamma phase when heated in the presence of the surfactant at 1°/min to 176 °C. Films without the additive, subjected to the same thermal treatment, melt and recrystallize in the alpha form when cooled. X-ray diffraction is the most convenient means of distinguishing between the two crystal phases. (IR and DSC are less definitive.) Films of alpha and gamma phases were subjected to the same poling conditions, and the piezoelectric and pyroelectric responses were measured. The much larger response from gamma phase for all electric fields less than 1.25 MV/cm confirms that this is a polar crystal phase. The value of 1.3 nC/cm^2K for pyroelectric coefficient after poling for 10^3 seconds at 80° and 1 MV/cm is almost the same as that reported for unoriented beta phase obtained by pressure quenching and poled at the same field for one hour at 23 °C. For values of electric field 750 kV/cm and greater, the alpha phase undergoes the electric field induced phase transition to a polar form, so that at 1.25 MV/cm the responses from alpha and gamma phase films are comparable. It has not been possible to pole at fields greater than 1.25 MV/cm because of electrical breakdown. In the course of this investigation we discovered that simply orienting the polymer film reduces electrical conductivity by more than a factor of 100. An improvement in electrical breakdown strength is indicated but not fully quantified at this time. Because of the field-induced phase transition of alpha phase, there seems to be no practical advantage for promoting the formation of gamma phase unless one must be confined to low poling fields. A detailed report on these results in in preparation.

We have also poled PVDF as it undergoes the alpha to gamma phase transition in the vicinity of 176 °C for the purpose of studying the stability of the resultant piezoelectric film. Unfortunately, the breakdown strength at these temperatures is about 400 kV/cm so that only low activity is achieved, and the response resulting from these low poling fields decays with time even at room temperature.

We have recently succeeded in increasing the piezoelectric and pyroelectric charge response (as opposed to voltage response) of PVDF by improving the coupling between the polar crystals and the external electrodes. A 0.1 M solution of tetrabutyl ammonium bromide in dichloroethane was diffused into a poled film which greatly increases the conductivity of the film. The initial pyroelectric activity of 2.4 nC/cm^2K increased to 3.3 nC/cm^2K. (Solvent without the electrolyte has no effect.) As the volatile solvent is removed, the response returns to its initial value but can be increased again by the sorption of dichloroethane from the vapor phase. A more highly poled sample subjected to similar treatment increased from an initial value of 3.3 nC/cm^2K to a maximum value of 4.4 nC/cm^2K. When the exposure time to the electrolyte solution was increased from 1 day to 3 days at 23 °C, the activity as we measure it was greatly reduced, presumably because the impedance of the polymer film becomes comparable to or less than that of the measuring circuit. Preliminary experiments using the same salt in the much less volatile 1,6-dichlorohexane have shown similar enhancements without loss of the enchanced activity with subsequent storage time at ambient conditions. These investigations are continuing.

In the past year we published a summary of a cooperative six-site model for ferroelectric switching in β-phase PVDF. This model predicts the essential features of polarization and IR transmission hysteresis curves and data on crystal plane reorientation with applied field. These data all apply to changes that occur well below the order-disorder (or Curie) transition implicit in the model and occurring in PVDF well above the melting point. This past year, Dr. Furukawa published data on a copolymer of PVDF and trifluoroethylene which showed a Curie temperature at 70 °C. It was possible then to extend the model calculations to the transition region. The experimental observation that the critical switching field decreased with increasing temperature and vanishes at 70 °C is consistent with the model, as is the anomalously high dielectric constant which has a maximum of about 70 at 70 °C. Using structural information, this dielectric constant anomaly was calculated for the six-site model. As expected, the calculated dielectric constant for the crystal phase was considerably larger than that for the semicrystalline sample. This occurs in any composite since the lower dielectric constant component reduces the electric field in the higher dielectric constant component. Because the particle shapes and orientations are so important in composite dielectrics, we are not able to calculate exactly what the semicrystalline sample dielectric constant is, even if we know the dielectric constants of the components. However, it looks as if there are some significant trends in the data not predicted by the model. A complete publication of the calculations to date is in preparation.

Automated Dielectric Measurement
Subtask 4 of Task 12139

F. I. Mopsik, S. J. Kryder, S. C. Roth

The automated dielectric spectrometer is nearing completion. This instrument will record the transient response of a dielectric sample in real time and using numerical transforms will automatically determine the dielectric constant and loss of the sample over the frequency range of 10 kHz to 0.001 Hz or below. The instrument should have a resolution of 10^{-5}, which is an order of magnitude improvement over most designs. This will allow determination of the dielectric properties of low loss polymers with much greater speed than previously possible.

Work done in FY80 includes completion of the charge detector. This detector can resolve 0.1 pC with a 10 μs rise time and for time up to 100 s. A major challenge that was overcome was the design of a reset circuit so that the output could be zeroed with negligible charge transfer or drift. In addition, the final interface boards have been acquired. Currently, the computer interconnections are being made prior to testing as a complete unit.

In addition, some of the programming for data treatment has been tested by its use with the thermal pulse experiment. In particular, the idea of data selection and interpolation for optimal computation has been successfully incorporated in the thermal pulse experiment and will be used in the spectrometer. This allows the actual data sampling to be done in an experimentally convenient manner with a sufficient excess of points to obtain significant noise reduction.

ASTM Activities
Subtask 5 of Task 12139

W. P. Harris

Mr. Harris chaired the final meeting of his six-year chairmanship of ASTM Committee D-9, Electrical Insulating Materials, at Dearborn in October 1979. There he received an award of appreciation for his excellent service. He attended the March 1980 ASTM meeting in Dallas and continues to serve as a member of the executive committee. Current activity in D-9 consists of revising D-150, which is one of the Committee's most widely used and cited testing documents.

Polymer Sensors for NDE
Subtask 6 of Task 12139

S. Edelman, S. C. Roth

The 1980 NDE work of the Electrical Properties Group consisted of the use of polymer sensors to measure dynamic elastic moduli and to detect wear in airplane control cables.

Making use of the sensitivity, low density, and flexibility of piezoelectric polymer strain gauges, we have worked out a non-resonant method for measuring both the real and imaginary parts of both the dynamic Young's modulus and the dynamic shear modulus of structural materials in the form of long, thin rods. All four quantities can be obtained as continuous functions of both frequency and static load. The frequency can be varied over a wide range, and the static load can be varied from a large compressive value through zero to a large tensile value.

The method can be used to study the basic dynamic properties of materials. It should be especially useful in studying composite materials and polymers, materials whose dynamic properties are likely to vary with static load. In the case of composite materials, variation of damping characteristics with static load can be expected to be a sensitive test of the quality of the bonding between components. The method can be used to provide basic engineering data needed for designing structures which are to be subjected to dynamic stresses or for which particular levels of internal damping must be obtained.

Since all measurements are made on a single specimen under identical conditions (except for the type of excitation) any deductions about the internal structure are free of the uncertainties introduced where measurements at different frequencies require different specimens and where measurements of the different moduli require different apparatus. The method can be used for nondestructive evaluation of structural elements either for compliance with design specifications or for monitoring a change in properties during service. A paper describing the method was presented at the April 1980 meeting of the Acoustical Society of America. Support for a laboratory installation to apply the method is being sought.

The study of airplane control cables is being performed on an apparatus in which the cable, under tension, is pulled around a small pulley by a cam which converts the rotation of an electric motor to reciprocating motion. A polymer sensor, attached to the cable near the pulley, detects the noise of the motion of the strands as they deform on the pulley. The sensor can be removed from the cable and reattached readily so that the same sensor can be used to compare different cables or different conditions. An elaborate mechanical filter eliminates motor noise from the signal. A spectrum analyzer operates on the sensor signal, and changes in the spectrum are monitored to detect the effects of fatigue and wear.

Polymer Stress Gauge For Intaglio Printing Press
Subtask 7 of Task 12139

M. G. Broadhurst, S. C. Roth, S. J. Kryder, A. S. DeReggi, S. Edelman

This work, which is supported by the Bureau of Engraving and Printing, U.S. Department of Treasury, involves the development of a gauge to measure the dynamic pressure at critical points in the presses used to print money. The first phase of the work was completed last year. The accomplishments of the first phase included measurement of the width of the area of contact between the two cylinders of the press, the duration of contact of a point on the upper cylinder with the lower cylinder, and a qualitative (uncalibrated) determination of the change of the pressure with time during contact.

This year work began on the second phase which is to provide calibrated pressure measurements. Specifications for telemetry have been written and equipment ordered. Dedicated data processing equipment has also been ordered. Preliminary design and construction of polymer gauges is well along. A start has been made on design of a field calibrator for checking the calibration of pressure gauges after installation.

Ultrasonic Hydrophone
Subtask 8 of Task 12139

A. S. DeReggi, S. C. Roth, J. M. Kenney, S. Edelman

This project is partly sponsored by the Bureau of Radiological Health, which is contributing the services of a guest worker. One objective of the project is to develop a piezoelectric polymer hydrophone for characterizing, point-by-point, the acoustic field beamed by ultrasonic transducers, such as those used in biomedical equipment. Accurate knowledge of the details of the acoustic field is not otherwise obtainable. The knowledge can be used to ensure both the safety and adequacy of ultrasonic dosage and for research in ultrasonic treatment.

During this year, the performance of several prototype hydrophone probes has been investigated thoroughly, with regard to both frequency response and performance stability at room temperature. The sensitivity, the broadband responsivity, the non-perturbing properties, and the long-term stability have been judged good enough for the Bureau of Radiological Health to adopt the probe as a standard probing hydrophone. A paper is currently under review for publication in the Journal of the Acoustical Society of America. In addition, a patent is being sought.

Several prototype annular arrays have been constructed and tested. These arrays consist of concentric ring-detectors formed as common parts of a tensioned polymer membrane. They are being used in ultrasonic research to verify ideas in the theoretical modeling of disc-shaped ultrasonic projectors. The geometry of the polymeric arrays allows the measurement with unprecedented precision of the relative contribution of the ring diffraction term and the piston plane wave term of the projected acoustic beam. This work is the subject of the Ph.D. dissertation of our guest worker, Gerald Harris of the Bureau of Radiological Health, who is also a part-time student at Catholic University. A preliminary account of this work has been submitted for presentation at the 25th Annual Meeting of the Institute of Ultrasound in Medicine in New Orleans on September 15-19, 1980, and for publication in the Proceedings of that Conference.

Durability of Piezoelectric and Pyroelectric Activity in PVDF
Subtask 9 of Task 12139

J. M. Kenney, M. G. Broadhurst

This work was initiated with the Naval Undersea Systems Command because of their interest in widespread use of polymer hydrophones by the U.S. Navy. Since good durability of activity is crucial for this application and since long time testing makes it difficult to judge the effects of structural or processing modifications on durability, we have developed a short time test procedure which will give a rapid measure of relative durabilities of different samples. The test consists of continuously recording pyroelectric activity while the temperature is being increased linearly to the melting point of the sample. Samples show a broad maximum in activity vs. temperature. We use the temperature at which the activity falls as a measure of durability--the higher the temperature the more durable the sample.

Dramatic differences were seen between samples of PVDF and a copolymer of PVDF with tetrafluoroethylene. The temperature at which the activity falls to zero is 100 °C for the copolymer and 170 °C for the PVDF.

While this short time test will be useful for comparing effects of different structures and treatments, it must be calibrated with longer time aging studies. This year we made measurements of 38 PVDF samples which had been stored at room temperature for 15 months. It was found that the activity of the specimens as a fraction of the initial activity was 0.91 ± 0.05. The magnitude is similar to that measured at two DOD laboratories in previous studies.

The mechanism of loss of activity of PVDF has not yet been established, and these measurements should provide valuable data for the development of a suitable aging model.

Space Charge Studies
Subtask 10 of Task 12139

A. S. DeReggi, F. I. Mopsik, M. G. Broadhurst

The static and kinetic effects of space charge in polymers subjected to electric fields continues to be of interest as different groups in the USA and outside are developing new methods to measure these effects. In the poling of piezo- and pyroelectric polymers where near-breakdown fields are applied temporarily and in the standing-off of high potentials by polymeric electrical insulation where moderate fields are sustained for extended periods of time, space charge is either initially present as an ionic impurity, is produced through field-enhanced degradation, or is injected across the electrode-polymer interface. The space charge typically distorts the applied electric field and gives rise to regions of field concentration. In the case of insulation, there is a resultant acceleration of the aging process leading to premature breakdown. In the case of piezoelectric polymers, there is a resultant non-uniform distribution of polarization which in combination with a small but finite conductivity gives rise to unusual transduction phenomena.

Until recently, only qualitative information was obtained about the space charge and polarization distributions because of the preliminary stage of development of the methods used to measure these distributions. For example, using the thermal pulse method we were able to show that in PVF subjected to a poling voltage, polarization tends to reside near the negative poling electrode for a wide range of poling voltages and poling times and furthermore, that a threshold mean field of $\sim$ 150 V/μm must be exceeded in order for significant remnant polarization to be found. Extremely weak remnant polarization was measured for mean fields as low as 24 V/μm. We suppose that positive space charge plays an important role in producing a distribution of electric fields in the sample and hence a distribution of applied poling fields. These observations are markedly different from those made on PVDF where polarization tends to reside near the positive poling electrode (presumably due to negative space charge) and where there is a more gradual increase in remnant polarization as a function of the mean applied field. A paper discussing the role of space charge on the poling behavior of PVF has been written with a recent guest worker, Professor Sidney Lang of the Ben Gurion University (Israel), and has been submitted for publication in Ferroelectrics.

We have recently been able to acquire the transient charge response from the thermal pulse experiment in digital form, and the computer programming for data analysis has been completed and tested. From the data, one extracts the coefficients of a Fourier series representing the polarization distribution in the film. When data can be obtained by illuminating first one side of the film and then the other, the sum and difference of the two signals yield only even or only odd Fourier coefficients.

This separation of terms facilitates a good determination of the thermal time constant τ for the sample. An important feature of the program is that data are not chosen at equal increments of time but are taken at times chosen to yield the most information about the relaxation time of the nth term which varies as τ/n^2. When data are available by pulsing alternate sides of the film, as many as ten Fourier coefficients can be determined. This means, very roughly, that the "resolution" is about one-tenth of the film thickness. This amount of detail in the charge and/or polarization distribution is expected to be of great value in directing the development of models for non-uniform field distribution during the early stages of poling.

Piezoelectric Polymer Fuzing
Subtask 11 of Task 12139

S. C. Roth, A. S. DeReggi, S. Edelman

This project is sponsored by the U.S. Army Armament Research and Development Command. It is developed from previous work by NBS in cooperation with Frankford Arsenal reported in NBSIR 75-724 (R). NBS is to assist ARRADCOM to determine the feasibility of using piezoelectric polymer film in impact sensors for fuzing applications in several particular geometries.

An equation was developed describing the performance of piezoelectric polymer in fuzing. When reasonable values, supported by the results of impact studies, were used in the equation, it was predicted that sufficient energy would be released to detonate a 105 mm high energy antitank round.

A technique using heat, vacuum, and pressure was developed for shaping piezoelectric polymer to the inside of an ogive (forward part of a munitions casing). An ogive instrumented in this way was delivered to ARRADCOM for testing.

A draft of the final report has been sent to ARRADCOM for comment and approved by them.

Development of Piezoelectric Polymer Stress Gauges for Rock Studies
Subtask 12 of Task 12139

S. C. Roth, S. Edelman

This work, funded by the Denver Mining Research Center of the Bureau of Mines, is a continuation of work described in the report for last year to measure noise from grinding together of rock specimens.

Most of a series of polymer gauges for measuring rock noises were developed at NBS and delivered last fiscal year. The remaining gauges have been constructed and will be delivered this fiscal year. The gauges have been effective in detecting and measuring the acoustic emission from rock samples under stress. Also, they have been found to survive collapse and crushing of the rock specimens unless a crack develops directly across the active area. Future work on rock and soil transducers is expected to result from tests on these transducers.

Thick Electrode Transducers
Subtask 13 of Task 12139

A. J. Bur, M. G. Broadhurst

The fabrication of transducer specimens of PVF_2 with thick, well adhering electrodes was attempted. The objective was to study the influence of the mechanical properties of the electrodes on the PVF_2 transducer behavior. It is expected that the hydrostatic response will be enhanced by a factor of two to three if the electrodes maintain their own integrity and exert a stress on the polymer film during temperature and/or pressure changes. Transducers previously fabricated in our laboratory have had very thin evaporated electrodes, several hundred angstroms thickness. Because the electrode is so thin, the mechanical properties of the polymer substrate dominate.

Metals such as Ni, Au, Ag, and Cu have elastic moduli which are 30 to 40 times larger than that of PVF_2. A metal electrode of 0.4 μm thickness will have the same rigidity as 12 μm of PVF_2. A metal electrode of 4 μm thickness will have 10 times the rigidity of the polymer. Relative to the polymer, a thick electrode can be considered rigid so that when the polymer contracts, a stress between electrode and polymer develops. The predicted effect of this stress is to enhance the change in the thickness of the polymer film by a factor of two or three relative to the change with thin electrodes.

Previous attempts to detect a significant electrode thickness effect have been unsuccessful, presumably due to poor adhesion between polymer and metal. This year we have made measurements on a series of specimens furnished by Bell Telephone Laboratories which showed a systematic dependence of piezoelectric response due to stretching in the plane of the film with different thicknesses of gold making up the electrodes. As in previous studies, we have yet to find a large difference (more than 10-20 percent) in pyroelectric response or hydrostatic piezoelectric response before and after the gold electrodes are removed. The differences we see in the activity of these specimens with electrode thickness seem to be due in part to differences in sample polarization.

We suspect that stiff electrodes inhibit polarization of these films by restricting the local strains needed to accommodate changes in crystal phase and orientation which occur as part of the poling process. We are presently conducting experiments to measure this polarization for specimens with differing electrode stiffness to characterize this effect. We are making sure that the polarization measurements made during poling agree with those made while the specimens are depoled (melted) and will then depole the Bell Lab specimens to determine their state of polarization.

As a final attempt to measure thick electrode effects, we have arranged to obtain samples from EMI with well attached electrodes of differing thickness. If these do not show the expected effects, we will be forced to conclude that the effect does not exist, though no explanation for its absence has yet been found.

Fabrication of Piezoelectric Polymer Film
Subtask 14 of Task 12139

A. J. Bur, M. G. Broadhurst

The Department of the Navy is supporting a project to fabricate piezoelectrically active PVDF specimens with thicknesses of 0.79 mm (31 mil). A thick transducer is desired because it will have a lower capacitance than the thin film PVDF transducers which we have routinely prepared and a correspondingly higher voltage response for a given strain.

The problems with making thick polymer transducers are the large stresses needed to stretch thick samples and the large voltages needed to apply a polarizing field to them. Large Instron machines were used to stretch our materials while the high voltage group at NBS assisted in poling them. Initial failures at poling thick samples were due to low breakdown strength which we suspected was an inherent disadvantage of thicker, more defect prone samples. Further investigation, however, showed that there was a large difference between oriented and unoriented material. The oriented material is able to withstand poling fields of 1 MV/cm so that acceptable transducer activity can be achieved. We have not established the quantitative difference in breakdown strength between unoriented and oriented PVDF, but qualitatively it can be concluded from these observations that such a difference exists.

To better understand this dependence of breakdown strength on stretching, we measured the resistivity of stretched and unstretched PVDF from several sources. The data distinctly show that the resistivities for unoriented PVDF are lower than those for the oriented material by at least an order of magnitude. While we have not established a relationship between resistivity and breakdown strength, we conclude that the state of orientation is an important factor which affects the electrical properties of PVDF.

Molecular orientation is extremely important to making successful thick polymer hydrophones. These thick hydrophones are equal to, and may exceed, the performance of present state-of-the-art ceramic hydrophones. The use of this effect to study the basic nature of conduction is equally important scientifically.

Diffraction From Nonperiodic Structures: The Molecular Conformation of Polytetrafluoroethylene (Phase II)
Subtask 15 of Task 12139

E. S. Clark[1], J. J. Weeks, R. K. Eby

[1]University of Tennessee

The crystal structure of polytetrafluoroethylene has been a subject of discussion among spectroscopists, crystallographers, and others. However, the determination of structure in synthetic polymers is made difficult by the lack of resolution in the diffraction data. The diffuseness of the reflections observed in most x-ray fiber patterns results from the small size, misorientation, and imperfect lattice nature of the crystallites. This lack of resolution leads to poor accuracy in measurement of peak position and makes determination of layer line heights difficult with a corresponding loss of significant figures in evaluation of the repeat distance for the molecular conformation. In helical conformations, the repeat distance may be of considerable length or indeterminate and, in effect, nonperiodic. Remarkable electron diffraction patterns of the low temperature form of polytetrafluoroethylene have been obtained which exhibit layer lines sharply resolved to the 26th order. These patterns permit accurate measurements of the layer line heights. Equations have been developed to relate these heights to a molecular conformation defined in terms of an incommensurable helix of ratio, $r = u/t$, defining a conformation of u motifs regularly spaced along t turns of the helix. The electron diffraction data yield a molecular conformation of $r = u/t = 2.159$, with the molecule slightly untwisted from the previously assigned conformation of $r = 13/6 = 2.167$. The newly determined conformation corresponds within the limits of error to $r = 948/439$. However, the practice of expressing a helical conformation in terms of some commensurable ratio, u^*/t^*, is questionable. If the helical conformation is not expressed accurately in terms of simple <u>small</u> numbers, it is preferable to define the conformation in terms of the ratio, r, limited to the number of significant figures. This point is made tellingly in the present case where a change of one standard deviation in r changes u^*/t^* from 948/439 to 54/25. Furthermore, the error limits admit 82 other possibilities for $t^* < 500$.

Order-Disorder Transitions in Polytetrafluoroethylene
Subtask 16 of Task 12139

J. J. Weeks, I. C. Sanchez, C. I. Poser[1], R. K. Eby

[1]Guest worker, University of Massachusetts

The phase diagram of polytetrafluoroethylene has been enlarged by differential scanning calorimetry to include the concentration of hexafluoropropylene comonomer units. The two transitions near 292 and 303 K in the homopolymer move to lower temperatures with increasing concentration and apparently become one at a small concentration. Analysis of the data for this single transition yields 295 K for the temperature and

13.2 J/g for the heat of transition of an infinitely large homopolymer crystal. The heat of transition associated with the formation of a crystal defect is 0.021 eV. The qualitative features of the transitions can be accounted for by a mean-field model which involves two order parameters corresponding to planar units and helix reversals. This model yields two transitions which move closer together and to lower temperatures with increasing comonomer concentration. Decreasing lamellar thickness will have a qualitatively similar effect.

Other Activities of the Polymer Science and Standards Division

Invited Talks

Experiments on Non-Linear Elasticity
Short Course on Continuum Mechanics, NBS, Gaithersburg, Maryland
E. A. Kearsley
July, 1979

Dental Materials--Their Selection and Handling Techniques in 1979-80
Travis Air Force Base, Solano, California
N. W. Rupp
September 5, 1979

Crystal Disorders in Copolymers of Tetrafluoroethylene and Hexafluoropropylene
American Chemical Society, Washington, D.C.
R. K. Eby, E. S. Clark, and J. J. Weeks
September 12, 1979

Dental Materials--Their Selection and Handling Techniques in 1979-80
Scott Air Force Base, Saint Clair, Illinois
N. W. Rupp
September 12, 1979

Molecular Interpretation of the Load-Elongation Curve of Crystalline Polymers
ACS Symposium on Stress-Cracking of Plastics, Washington, D.C.
A. Peterlin
September 14, 1979

Transport Phenomena and Polymer Morphology
IUPAC Symposium on Polymers, Mainz, West Germany
A. Peterlin
September 18, 1979

Seminar on Clinical Research
University of Minnesota, Minneapolis, Minnesota
N. W. Rupp
September 18, 1979

Raman Frequencies and Intensities of Longitudinal Acoustic Modes of Polymers
University of Massachusetts, Amherst, Massachusetts
B. M. Fanconi
September 21, 1979

Operating Techniques With Recently Introduced Dental Materials
University of West Virginia, Morgantown, West Virginia
N. W. Rupp
September 21, 1979

Application of Varied Heating Rate Methods to Polymer Degradation Reactions
Ninth North American Thermal Analysis Society Conference, Chicago, Illinois
J. H. Flynn
September 25, 1979

Polymer Morphology and Chain Transport Mechanisms
Boris Kidric Institute of Nuclear Sciences VINCA, Belgrad, Yugoslavia
D. H. Reneker
September 25, 1979

Recent Developments in Dental Materials and Their Handling Techniques
Lackland Air Force Base, San Antonio, Texas
N. W. Rupp
September 27, 1979

Properties of Polymers Including Chain Transport and Piezoelectric Effects
Josef Stefan Institute, Ljubljana, Yugoslavia
D. H. Reneker
September 28, 1979

The Diversity in the Habits Exhibited by Polymer Crystals Grown From Solution
Leeds University, Leeds, England
F. A. Khoury
October 2, 1979

Dynamic Scattering From Polymer Solutions
University of Michigan, Ann Arbor, Michigan
C. C. Han
October 5, 1979

Non-Linear Behavior of Viscoelastic Rubbers
Firestone Research Laboratories, Akron, Ohio
L. J. Zapas
October 12, 1979

Type II Diffusion in Glassy Polymers
Laboratory Technology of Polymers and Rheology, Naples, Italy
A. Peterlin
October 19, 1979

Order-Disorder Transitions in Polytetrafluoroethylene: Experiment and Theory
Institute of Basic Technical Problems, Warsaw, Poland
R. K. Eby
October 22, 1979

Impregnation and Void Filling of Porous Polymer Tape With Dielectric Oil
Conference on Electrical Insulationand Dielectric Phenomena, White Haven, Pennsylvania
A. J. Bur
October 23, 1979

Transport Phenomena and Polymer Morphology
Laboratory Technology of Polymers and Rheology, Naples, Italy
A. Peterlin
October 23, 1979

Ferroelectric Polarization in Polymers
Conference on Electrical Insulation and Dielectric Phenomena, White Haven, Pennsylvania
M. G. Broadhurst and G. T. Davis
October 24, 1979

The Structure and Transitions in Copolymers of Tetrafluoroethylene and Hexafluoropropylene
Polish Academy of Sciences, Lodz, Poland
R. K. Eby
October 24, 1979

Crystal Disorders in Copolymers of Tetrafluoroethylene and Hexafluoropropylene
Institute of Polymer Chemistry, Zabrze, Poland
R. K. Eby
October 26, 1979

Elastic Modulus and Strength of Highly Drawn Polymers
Dutch Staatsmijnen, Geelen, Holland
A. Peterlin
October 26, 1979

Non-Linear Viscoelastic Behavior of PMMA in Torsion
Bell Telephone Laboratories, Murray Hill, New Jersey
G. B. McKenna
October 26, 1979

A History of the Society of Rheology
Fiftieth Anniversary Meeting of the Society of Rheology, Boston, Massachusetts
R. S. Marvin
October 29, 1979

Polymers as Piezoelectric Elements
Plastics Institute of America, Hoboken, New Jersey
M. G. Broadhurst
November 1, 1979

Statistical Mechanical Models of Polymers and Their Solutions
Massachusetts Institute of Technology, Cambridge, Massachusetts
I. C. Sanchez
November 7, 1979

Diffusion and Determination of Chain Structure in Polymers
Georgetown University, Washington, D.C.
L. E. Smith
November 7, 1979

Overview of Investigations in the Polymers Division on "The Structure and Dielectric Properties of Polymer Tape Insulation for High Power Transmission Cables"
Battelle Laboratories, Columbus, Ohio
F. A. Khoury
December 6, 1979

Phase Equilibrium Behavior of Polymer Blends
University of Akron, Akron, Ohio
I. C. Sanchez
December 6, 1979

Application of Solid State ^{13}C NMR in Semicrystalline Polymers
Firestone Tire & Rubber Co., Akron, Ohio
D. L. VanderHart
December 20, 1979

Piezoelectric and Pyroelectric Properties of Polymers With Applications
International Business Machines, Binghamton, New York
M. G. Broadhurst
January 28, 1980

Piezoelectric and Pyroelectric Polymers--Mechanisms and Applications
University of Virginia, Charlottsville, Virginia
G. T. Davis
January 28, 1980

Concentration Dependence of Polymer Chain Dimensions
Johns Hopkins University, Baltimore, Maryland
D. J. Lohse
January 30, 1980

Phase Diagrams of Polymer Blends
Great Lakes Polymer Conference, Wayne State University, Detroit, Michigan
I. C. Sanchez
February 14, 1980

Theory of Polymer Interfacial Tension
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware
I. C. Sanchez
February 14, 1980

Molecular Weight and Temperature Dependence of Polymer Dimensions and Intrinsic Viscosity
University of Massachusetts, Amherst, Massachusetts
C. C. Han
February 15, 1980

Statistical Mechanical Models of Polymers and Their Solutions
Michigan Molecular Institute, Midland, Michigan
I. C. Sanchez
February 15, 1980

Dependence of Chain Dimensions on Concentration
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware
D. J. Lohse
February 18, 1980

The Development of Test Methods for the Environmental Stress-Crack Resistance of Ethylene Plastics
ASTM Subcommittee D-20.10.14, San Diego, California
J. M. Crissman
February 19, 1980

Statistical Mechanical Models of Interacting Polymer Chains
NBS Colloquium on Mathematical Modeling in Science and Engineering, Gaithersburg, Maryland
I. C. Sanchez
February 20, 1980

Diversity in the Lateral Growth Habits and Non-Planar Character of Polyethylene Crystals
Bell Telephone Laboratories, Murray Hill, New Jersey
F. A. Khoury
February 21, 1980

Dependence of Polymer Chain Dimensions on Concentration
Hercules Corporation, Wilmington, Delaware
D. J. Lohse
February 21, 1980

Methods for Testing the Validity of Kinetic Models Using Data From Varied Heating Rate and Jump Techniques
American Chemical Society, Seton Hall Univ., South Orange, New Jersey
J. H. Flynn
February 25, 1980

Polymer Coil Instability in Laminar Flow
American Chemical Society, Carnegie-Mellon University, Pittsburgh, Pennsylvania
A. Peterlin
February 28, 1980

Statistical Thermodynamics of Polymer Solutions
Johns Hopkins University, Baltimore, Maryland
I. C. Sanchez
March 5, 1980

^{13}C Linewidths in Solid Polymers Using High-Power Proton Decoupling and Magic Angle Sample Spinning
21st Experimental NMR Conference, Tallahassee, Florida
D. L. VanderHart
March 17, 1980

Interfacial Tension Theory of Polymer Solutions
University of Washington, Seattle, Washington
I. C. Sanchez
March 18, 1980

Phase Diagrams of Polymer Alloys
Washington State University, Pullman, Washington
I. C. Sanchez
March 19, 1980

Piezoelectric and Pyroelectric Applications of Plastics
American Chemical Society, Houston, Texas
M. G. Broadhurst
March 24, 1980

Poling Behavior of PVDF
American Physical Society, New York, New York
M. G. Broadhurst and G. T. Davis
March 24, 1980

Piezo- and Pyroelectric Response From PVDF in Form III (γ)
American Physical Society, New York, New York
G. T. Davis and M. G. Broadhurst
March 24, 1980

Non-Uniform Polarization and Space Charge in Ferroelectric Polymers
American Physical Society, New York, New York
A. S. DeReggi and M. G. Broadhurst
March 24, 1980

Temperature Dependence of the Pyroelectric Response and Thermal Depoling of Vinylidene Fluoride Polymer
American Physical Society, New York, New York
A. S. DeReggi, G. T. Davis, and M. G. Broadhurst
March 24, 1980

Ferroelectric Polarization in Polymers
American Physical Society, New York, New York
M. G. Broadhurst and G. T. Davis
March 27, 1980

Acoustic Emission of Polymers During Crazing
American Physical Society, New York, New York
A. Peterlin
March 27, 1980

Overview of NBS and the Polymers Division
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware
R. K. Eby
April 2, 1980

Dependence of Polymer Chain Dimensions on Concentration
Kansas State University, Manhattan, Kansas
D. J. Lohse
April 4, 1980

Statistical Mechanics of Polymer Solutions
Exxon Chemical Co., Linden, New Jersey
D. J. Lohse
April 8, 1980

Re-Evaluation of the Safety of Plastics
North Carolina State University, Raleigh, North Carolina
L. E. Smith
April 9, 1980

Mechanical Durability and Failure of Polymeric Materials
Free University, Amsterdam, Netherlands
G. B. McKenna
April 14, 1980

A Mean Field Theory of Polymer Solutions
Polytechnic Institute of New York, Brooklyn, New York
D. J. Lohse
April 15, 1980

Time Dependent Failure in PMMA and Polyethylene
University of Manchester Institute of Science and Technology, Manchester, England
G. B. McKenna
April 16, 1980

Time Dependent Deformation and Failure Behavior of Poly(Methyl Methacrylate) and Polyethylene
University of Leeds, Leeds, England
G. B. McKenna
April 17, 1980

Response of Carbon Black Filled Rubber to Cyclic Loading
Malaysian Rubber Products Research Association, Brickendonberry, England
G. B. McKenna
April 18, 1980

Measurement of Dynamic Elastic Moduli
99th Acoustical Society, Atlanta, Georgia
S. Edelman
April 22, 1980

Piezoelectric and Pyroelectric Polymers: Mechanisms and Applications
Mechanics and Materials Colloquia, Rutgers University, New Brunswick, New Jersey
G. T. Davis
April 24, 1980

Statistical Mechanics of Dilute and Semi-Dilute Polymer Solutions
Carnegie-Mellon University, Pittsburgh, Pennsylvania
I. C. Sanchez
May 2, 1980

Transport Phenomena in Drawn Semicrystalline Polymers I
Laboratory Technology of Polymers and Rheology, Naples, Italy
A. Peterlin
May 7, 1980

Cyclic Creep and Failure of Carbon Black Filled Rubber
IBM Research Laboratories, San Jose, California
G. B. McKenna
May 9, 1980

Transport Phenomena in Drawn Semicrystalline Polymers II
Laboratory Technology of Polymers and Rheology, Naples, Italy
A. Peterlin
May 12, 1980

Tensile Failure of Semicrystalline Polymers
U.S.-Japan Meeting on Crazing, Flow, and Forming of Polymers, Rutgers University, New Brunswick, New Jersey
A. Peterlin
May 21, 1980

Perspectives on Resolution for ^{13}C NMR in Solid Hydrocarbons Using Magic Angle Spinning
University of Delaware, Newark, Delaware
D. L. VanderHart
May 22, 1980

Research and the Saving of Teeth
Tokyo Medical and Dental University, Tokyo, Japan
G. C. Paffenbarger
May 30, 1980

Dental Alloy and Ceramic Compatibility
International Precious Metals Institute, Toronto, Canada
J. A. Tesk
June 2, 1980

The Accelerative and Adhesive Bonding Capabilities of Surface Active Accelerators
International Association for Dental Research, Osaka, Japan
J. M. Antonucci
June 6, 1980

Derivatives of p-N,N-Dialkylaminophenylalkanoic Acid: New Accelerators for Dental Composites
International Association for Dental Research, Osaka, Japan
G. M. Brauer
June 6, 1980

Ferroelectric Polarization in Polymers
International Symposium on the Statistical Mechanics of Phase Transitions in Polymers, Case Western Reserve University, Cleveland, Ohio
M. G. Broadhurst
June 13, 1980

Piezoelectric Polymer Research at NBS
Piezoelectric Polymer Workshop, Naval Research Laboratory, Orlando, Florida
G. T. Davis
June 13, 1980

Research and the Saving of Teeth
Taiwan University of Dentistry, Taipei, Taiwan
G. C. Paffenbarger
June 13, 1980

Recent Developments With Piezoelectric Polymers
Polymer Chapter of the 3M Company Technical Forum, St. Paul, Minnesota
M. G. Broadhurst
June 16, 1980

Enhancing Fluoride Incorporation into Enamel
School of Dentistry, National Taiwan University, Taipei, Taiwan
W. E. Brown
June 16, 1980

An Equilibrium Thermodynamic Approach is Taken to Describe the Morphology and Stress Change During Crystallization or Melting
Gordon Research Conference on Polymer Physics, New London, New Hampshire
W.-L. Wu
June 25, 1980

Lifetime Prediction of Polymer Stabilization
Institute of Polymer Science and Technology, University of New York, New Paltz, New York
J. H. Flynn
June 27, 1980

High Resolution Solid State ^{13}C NMR of Semicrystalline Polymers
Gordon Conference on Fiber Science, New London, New Hampshire
D. L. VanderHart
June 30, 1980

Methods for Testing the Validity of Kinetic Models Using Data From Varied Heating Rate and Jump Techniques
Sixth International Conference on Thermal Analysis, Bayreuth, West Germany
J. H. Flynn
July 8, 1980

High Resolution Solid State ^{13}C NMR Techniques for Studying Orientation and Molecular Motion in Polymers
Gordon Conference on Polymers, New London, New Hampshire
D. L. VanderHart
July 8, 1980

Non-Equilibrium Thermodynamics of Perfect Elastic Fluids
Seminar on Thermodynamic Inequalities, NBS, Gaithersburg, Maryland
E. A. Kearsley
July 17, 1980

Polarization and Molecular Hysteresis in Polyvinylidene Fluoride
Gordon Conference on Dielectric Phenomena, New London, New Hampshire
M. G. Broadhurst
July 19, 1980

Scanning Transmission Electron Microscopy of Polyethylene Crystals
Electron Microscopy Society of America, Reno, Nevada
F. A. Khoury
August 4, 1980

The Strain-Energy Function for Rubber-Like Materials
IUTAM Symposium on Finite Elasticity, Lehigh University, Bethlehem, Pennsylvania
L. J. Zapas
August 11, 1980

Polymers in the Future
American Society for Mechanical Engineers Emerging Technology Conference,
San Francisco, California
R. K. Eby
August 15, 1980

Equation of State Theories of Polymer Blends
International Symposium on Polymer Compatibility and Incompatibility, Michigan Molecular Institute, Midland, Michigan
I. C. Sanchez
August 18, 1980

Spectral Resolution in Solid Hydrocarbons Using Magic Angle Sample Spinning ^{13}C NMR
NATO Advanced Study Institute, Cagliari, Italy
D. L. VanderHart
September 3, 1980

Solid State ^{13}C NMR in Polymers
NATO Advanced Study Institute, Cagliari, Italy
D. L. VanderHart
September 4, 1980

Concentration Effect on Polymer Chain Dimensions
Joint U.S.-France Conference on Small Angle Scattering, Strasbourg, France
C. C. Han
September 17, 1980

Piezoelectric Polymers
Office of Naval Research Meeting on Electroactive Polymers, Washington, D.C.
M. G. Broadhurst
September 29, 1980

Technical and Professional Committee Participation and Leadership

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Session Chairman

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Biological Mineralization Award Committee

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Washington Section Delegate

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Member: Meetings and Expositions Committee
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American Dental Association Acceptance Program

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Member: Porcelain Metal Alloys

American Institute of Physics

R. K. Eby
Section Editor, 1981 Physics Handbook

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Member: Committee for Public Policy

American National Standards Institute
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Mercury for Amalgams, Chairman
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Division of High Polymer Physics
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Committee on History of DMPP
Committee on Short Courses

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D02.07A: Newtonian Viscometry

D09: Electrical Insulating Materials
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Member: D09.05: Ceramic Products
D09.12: Electrical Tests
D09.16: Hookup Wire Insulation
D09.17: Thermal Capabilities
D09.90: Executive Committee
D09.93: Education, Research, and Symposia
D09.94: Nomenclature, Significance, and Statistics
D09.95: Liaison

D11: Rubber and Rubber-Like Materials
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Member

G. B. McKenna
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D20: Plastics
R. K. Eby, Chairman
Member: D20.01: Executive Subcommittee

J. D. Barnes
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D20.19: Sheeting
D20.70: Analytical Methods
WG.07: Gas Permeability

D. H. Reneker
Member

J. C. Smith
Member

H. L. Wagner
Member: D20.70: Analytical Methods
WG.04: Liquid Size Exclusion Chromatography
WG.05: Molecular Weight Parameters, Chairman

D27: Electrical Insulating Liquids and Gases
W. P. Harris
Member

E09: Fatigue
G. B. McKenna
Member

R. W. Penn
Member

E37: Thermal Measurements
S. S. Chang
Member: E37.01: Test Methods and Recommended Practices
E37.05: Thermophysical Properties

J. H. Flynn
Member: E37.03: Nomenclature and Definitions, Chairman
E37.90: Executive Subcommittee

E45: Geothermal Energy and Resources
E. A. Kearsley
Member: E45.02: Materials

F02: Flexible Barrier Materials
J. D. Barnes
Member: F02.30: Test Methods, Chairman
F02.93: Statistical Matters, Chairman

D. H. Reneker
Member

F04: Medical and Surgical Materials and Devices
G. M. Brauer
Member: F04.20: Resources
WG.01: Polymeric Materials, Chairman

J. M. Cassel
Member: F04.20: Resources

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Member

G. B. McKenna
Member

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R. K. Eby
Member

Chemical Society of Washington
G. M. Brauer
Chairman, Membership Activities

International Confederation for Thermal Analysis
J. H. Flynn
Member: Nomenclature Committee
Working Party on Symbols

International Electrotechnical Commission
TC046: Cables, Wires and Waveguides for Telecommunication Equipment
L. J. Zapas
Member: WG.03: Measuring Methods of Polyethylene

International Standards Organization
TC106: Dental Materials and Dveices
G. M. Brauer
Member: Task Force on Color Stability

N. W. Rupp
Member: Restorative Materials

National Bureau of Standards Advisory Panel for Tariffs on Electron Microscopes Under Florence Agreement

F. A. Khoury
Member

National Center for Small Angle Scattering

Users Committee

C. C. Han
Member

National Research Council Panel on Polymer Science and Engineering

R. K. Eby
Member

North American Thermal Analysis Society

J. H. Flynn
Member: Executive Committee
Publications Committee, Chairman

Polymer Degradation and Stability (Journal)

J. H. Flynn
Editorial Board Member

Sixth International Conference on Thermal Analysis

J. H. Flynn
Session Chairman

Society of Plastics Engineers

G. B. McKenna
Member: Technical Publications Committee

Society of Rheology

E. A. Kearsley
Member: Executive Committee

G. B. McKenna
Member: Committee on Education
Local Arrangements 1981 Spring Meeting, Chairman

University of Massachusetts Advisory Board on Polymer Research

R. K. Eby
Member

Publications

Optimizing Creep and Corrosion Properties in a Dispersant Amalgam Using Manganese
R. M. Waterstrat
J. Dent. Res., 57, 873 (1978)

New Initiator Systems for Dental Resins Based on Ascorbic Acid
J. M. Antonucci, C. L. Grams, and D. J. Termini
J. Dent. Res., 58, 1887 (1979)

Compatibility of Various Materials With Oral Tissues.
I: The Components in Composite Restorations
R. L. Bowen
J. Dent. Res. Special Issue, 58, 1493 (1979)

New Amine Accelerators for Composite Restorative Resins
G. M. Brauer, D. M. Dulik, J. M. Antonucci, D. J. Termini, and H. Argentar
J. Dent. Res., 58, 1994 (1979)

Bonding of Acrylic Resins to Dentin With 2-Cyanoacrylate Esters
G. M. Brauer, J. A. Jackson, and D. J. Termini
J. Dent. Res., 58, 1900 (1979)

Durability of the Bond Between Bone and Various 2-Cyanoacrylates in an Aqueous Environment
G. M. Brauer, J. W. Kumpula, D. J. Termini, and K. M. Davidson
J. Biomed. Mater. Res., 13, 593 (1979)

Storage Stability of Dental Composites
G. M. Brauer, N. Petrianyk, and D. J. Termini
J. Dent. Res., 58, 1791 (1979)

Polyvinylidene Fluoride Viewed as a Polycrystalline Ferroelectric Material
M. G. Broadhurst
Charge Storage, Charge Transport and Electrostatics With Their Applications,
Y. Wada, M. M. Perlman, and H. Kokado, Eds., p. 143 (1979)

General Comments, Session V, Third International Symposium on Tooth Enamel
W. E. Brown
J. Dent. Res. Special Issue B, p. 857 (1979)

Two Types of Pyroelectricity in a Copolymer of Vinylidene Fluoride as Tetrafluoroethylene
R. E. Collins, M. G. Broadhurst, G. T. Davis, and A. S. DeReggi
Charge Storage, Charge Transport, and Electrostatics With Their Applications,
Y. Wada, M. M. Perlman, and H. Kokado, Eds., p. 170 (1979)

Performance of Plastic Packaging for Hazardous Materials Transportation, Part V, Mechanical Properties
J. M. Crissman, L. J. Zapas, and G. M. Martin
NBSIR 79-1938 (1979)

Physical and Chemical Properties and Wear
G. R. Dickson
J. Dent. Res. Special Issue, 58, 1535 (1979)

Fit of Porcelain Fused-to-Metal Crown and Bridge Castings
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Michel Pineri
Centre d'Etudes Nucleaires, Grenoble, France
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I. H. Hall
University of Manchester, Manchester, England
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Derek G. Gray
McGill University, Montreal, Canada
September 14, 1979

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William J. MacKnight
University of Massachusetts, Amherst, Massachusetts
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Frank Karasz
University of Massachusetts, Amherst, Massachusetts
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R. E. Collins
New South Wales Institute of Technology, Sydney, Australia
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Brian C. Bowen
Princeton University, Princeton, New Jersey
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T. S. Subramanian
Washington State University, Pullman, Washington
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Andrew K. Jonscher
Chelsea College, University of London, London, England
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National Bureau of Standards, Washington, D.C.
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Stephanie L. Wunder
Naval Research Laboratory, Washington, D.C.
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Takeo Furukawa
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Gregory C. Farrington
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William Rostoker
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Field H. Winslow
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University of Tennessee, Knoxville, Tennessee
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B. B. Djordjevic
Johns Hopkins University, Baltimore, Maryland
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Carolyn K. Purvis
NASA-Lewis Research Center, Cleveland, Ohio
January 2, 1980

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Bruce Banks
NASA-Lewis Research Center, Cleveland, Ohio
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Henryk Eisenberg
Weizmann Institute of Science, Rehovoth, Israel
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Charles Rogers
Case Western Reserve University, Cleveland, Ohio
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Paul Mentag
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Shih-Jung Bai
University of Michigan, Ann Arbor, Michigan
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Marvin Bishop
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Keizo Matsuo
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D. L. Hunston
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Hans W. Spiess
Johannes-Gutenberg University, Mainz, West Germany
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Yvan Segui
University of Toulouse, Toulouse, France
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Christian Decker
Ecole Nationale Supérieure de Chimie de Mulhouse, Mulhouse, France
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G. Zerbi
Institute of Macromolecular Chemistry, Milan, Italy
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Pieter J. Lemstra
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Gerhard Zachmann
Institut für Anorganische und Angewandte Chemie, Hamburg, West Germany
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Gerhard Zachmann
Institut für Anorganische und Angewandte Chemie, Hamburg, West Germany
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Bernard Catoire
Institut Textile de France, Paris, France
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Michel Delsanti
Laboratoire Leon Billouin, Yvette, France
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Klaus Lederer
Institute for Chemistry and Physics, Leoben, Austria
July 3, 1980

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D. M. Sadler
University of Bristol, Bristol, England
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Twente University, Enschede, Netherlands
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Andrzej Ziabicki
Polish Academy of Science, Warsaw, Poland
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Werner Berger
Technische Universität Dresden, Dresden, East Germany
July 21, 1980

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Eric Goethals
University of Ghent, Ghent, Belgium
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Jakob Schelten
Institut für Festkörperforschung, Jülich, West Germany
August 13, 1980

External Recognition

Award of Appreciation
American Standards for Testing and Materials
October 1979
W. P. Harris

Charles Gordon Service Award
Washington Section
American Chemical Society
December 1979
G. M. Brauer

Silver Certificate
American Society for Metals
April 1980
J. A. Tesk

1980 Biological Mineralization Research Award
International Association of Dental Research
June 1980
W. E. Brown

Award of Appreciation
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R. K. Eby

Honorary Member
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J. M. Crissman
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American Standards for Testing and Materials, San Diego, California
J. D. Barnes
February 1980

METALLURGY DIVISION (564)

Robert Mehrabian, Chief
Anna C. Fraker, Deputy Chief
D. M. G. Summers, Secretary

The mission of the Metallurgy Division is to provide data, measurement methods, standards and reference materials, concepts, and information on the fundamental aspects of processing, structure, physical properties, and performance of metals and alloys to industry, Government agencies, and scientific organizations.

The program of the Division involves studies of metals and alloys in order to foster their safe, efficient, and economical utilization to meet our national needs within the larger framework of the materials cycle. Competences are developed and maintained in the general areas of chemical metallurgy with special emphasis on phase diagrams and phase stability; process metallurgy; quantitative microstructural characterization including nondestructive evaluation; properties including friction, wear, and the application of metals as synthetic orthopedic implants. The Division also makes a significant contribution as a national resource of metallurgical information through its Diffusion Data Center and Alloy Data Center. It provides consultation and assistance to other Government agencies and standards organizations in the development of necessary test methods and standards. The programs of the Metallurgy Division are designed to help us meet our future national needs for materials, which will depend in large measure on our response to forces which are now well recognized. Some of these are classical laws of supply and demand; others include such national problems as energy, environment, productivity, and such international problems as materials availability from third world nations.

For example, our Division, in addition to being involved in theoretical and experimental studies of phase stability, has a joint effort with the American Society for Metals to provide critically evaluated phase diagrams to the metallurgical community. Advancement in the understanding of phase diagrams and the development of predictive models for phase stability are essential in the development of new alloys for our future needs. These could include stronger and lighter alloys for the transportation industry to improve energy cost, new alloys specifically designed to exploit the beneficial effects of innovative new processes such as those referred to as rapid solidification processes, and alloys which would permit substitution of scarce or unavailable elemental constituents.

The detailed, programmatic content of the Division that follows is described in the four general task areas:

12142,51105	ALLOY STRUCTURE, PROPERTIES, AND STANDARDS FOR QUALITY CONTROL, and SYNCHROTRON RADIATION RESEARCH FOR MATERIALS SCIENCE
12143	METALLURGICAL PROCESSING FOR ALLOY DURABILITY
12144	ALLOY DURABILITY FOR WEAR APPLICATIONS
12145	CHEMICAL METALLURGY FOR DURABILITY

The technical activities under the various tasks are closely interrelated and address the overall mission of the Division to meet our present and future societal needs for metals. The central purpose of these scientific activities is to probe the relationships among processing conditions, the internal structure of metals, and their properties and performance. The resulting knowledge can be used to efficiently produce, shape, and otherwise process metals to control their properties and achieve the desired reliable and durable performance in the finished product.

Critical data compilations are being developed and delivered to users concerned with alloy properties, diffusion, and phase diagram information. Standard reference materials are being produced for electron microscope calibration, electron microprobe analysis, and electrical conductivity. Contributions are made to NBS programs in nondestructive evaluation, recycled oil and materials, and artificial implants.

Productive interactions with other groups at NBS exist in areas such as surface analysis, wear, microstructural characterization, acoustic emission, and phase diagrams. Computer graphics methods incorporating phase diagram predictive techniques and thermodynamic data are being developed in collaboration with the Applied Mathematics Division of the National Engineering Laboratory.

The results of our metallurgical research are communicated to the scientific community through technical publications, lectures, active participation of Division members on various national and international committees, personal contacts, and the organization and sponsorship of conferences and meetings on various subjects such as acoustic emission, synthetic implants, alloy phase formation, solidification, wear, and mechanical failure prevention. For example, the personnel in the Division serve on numerous ASTM Committees, including Chairman of the B-6 Committee and Post Chairman of Committee E-42, Vice Chairman of Committee G-2, and Chairman of several subcommittees. The technical staff have organized and chaired two international conferences on Rapid Solidification Processing, an international conference on Implant Retrieval: Material and Biological Analysis, and each year organizes and conducts two conferences on the prevention of mechanical failures, and is organizing the 1981 International Conference on Wear. The Metallurgy Division's staff serve on over sixty other national professional and technical committees.

The Metallurgy Division's programs also include direct contributions to industry through the NBS Research Associate Program. Extensive interaction with universities exists through the Cooperative Education Program, NBS Postdoctoral Program, and faculty guest workers. Considerable interaction also exists with other Government agencies, standards organizations, and the technical community at large. For example, the Division performs research for the following government agencies: the National Aeronautics and Space Administration, the Office of Naval Research, the Defense Advanced Research Project Agency, the Department of Energy, the Naval Ship Research and Development Center, the U.S. Army Materials and Mechanics Research Center, and the U.S. Army Mobility Equipment Research and Development Command.

The available competences in the Division have recently been strengthened and expanded by (1) a successful budget initiative in the area of metallic wear; (2) a new competence initiative within the National Bureau of Standards to develop research programs at the Synchrotron Light Source at Brookhaven National Laboratory with the main materials expertise to reside within the Metallurgy Division; (3) the addition of twelve new scientific staff members in the past twelve months; and (4) the development of new programs aimed at promoting technical innovation and improving our national productivity in the field of metals processing.

ALLOY STRUCTURE, PROPERTIES AND STANDARDS FOR QUALITY CONTROL
Task 12142, and

SYNCHROTRON RADIATION RESEARCH FOR MATERIALS SCIENCE
Task 51105

Innovative processing techniques are being developed to produce significant new microstructures and structural/property relationships. Coupled with increased industrial emphasis on quality control and automation, these require a range of microstructural characterization and nondestructive evaluation methods. The objectives of this task are to address this challenge by the development of measurement methods including nondestructive techniques and standards for the advanced quantitative characterization of metallurgical microstructures. These developments would permit automatic control methods for manufacturing and in-service use of industrial alloys. Methodologies include x-ray, optical and electron microscopy, eddy current, magnetic particles, positron annihilation, acoustic emission, and ultrasonic methods.

A new competence program in Synchrotron Radiation was initiated this past year (FY80) as a part of this task. The availability of intense tunable well-collimated radiation at synchrotron radiation facilities will permit radical gains in all areas of descriptive materials science, where the effects caused by the violation of translational invariance become increasingly important. As a joint NBS/NRL effort, we aim to establish an x-ray instrumentation complex at the National Synchrotron Light Source and to use it to perform frontier experiments in transformations in materials, kinetics studies, furtherance of x-ray optics, and the study of inner shell dynamics. One intermediate term goal of this effort is to establish an advanced x-ray analysis capability at Brookhaven and apply this to topographic analysis of cracks in a stressed metal alloy and to glass-crystal metal alloy transitions.

Other programmatic goals of this task are to evaluate quantitatively acoustic emission in steels and aluminum alloys and compare with theory, and to develop ultrasonic spectroscopy to the point that it can be used in microstructure characterization and quality control for defects during processing and use of structural alloys. Other efforts are aimed at developing new nondestructive evaluation (NDE) methods such as positron annihilation and in placing established techniques such as the magnetic particle method on a more quantitative and reproducible basis. New aluminum alloy eddy current standards were developed, calibrated, and issued under this task. Finally, the NML-SEM facility is located in this task. This facility not only serves various on-going research efforts, but also is used in the development of Standard Reference Materials for SEM.

The task is divided into subtasks whose activities and accomplishments over the past year are described next.

Synchrotron Radiation Research for Materials Science
Task 51105, and

Application of Synchrotron Radiation to Materials Science
Subtask 1 of Task 12142

M. Kuriyama, W. J. Boettinger, G. G. Cohen, R. D. Spal, H. E. Burdette

As the CMS part of the NBS program participating in the development of research programs at the Brookhaven National Synchrotron Light Source (NSLS), we have continued efforts on establishing beam lines on one of the two ports assigned to NBS and the Naval Research Laboratory (NRL) on the storage ring at NSLS. The beam lines of our concern will use hard radiation and will provide facilities for real time topography, small angle scattering, interface spectroscopy, and crystallography. Hard radiation down to as short as 0.5A will be produced from accelerated orbiting electrons in a storage ring operated at 2.5 GeV. Synchrotron radiation produces a spectrum of photons that is highly collimated, very intense, continuous in energy, and linearly polarized. These unique properties offer tremendous opportunities for advancing materials science with the following three major advantages over laboratory x-ray sources: (1) the approximately ten-fold increase in photon flux permits, for the first time, real-time *in situ* studies on materials transformations, (2) the tunability of available radiation for a desired energy permits determination of the phases of crystallographic reflections, thereby resolving important structural ambiguities. It also permits, via the elemental tunability, the study of materials whose structure deviates greatly from the periodicity locally, and (3) inelastic scattering could be employed for the first time as a practical tool to study materials properties and phase transitions via electronic properties of individual atoms and molecules in condensed matter. Among many problems aiming at the ultimate goal in materials science, which would be the formulation and verification of discrete atomistic theory for rates of phase transformations and structure stability, we have placed an emphasis at the initial phase on the development of dynamic *in situ* measurement capability to obtain an advanced knowledge in kinetics of microstructural transformations.

Under the new competence program started this past year (FY80), we have added Dr. Gabrielle G. Cohen and Dr. Richard D. Spal to our permanent professional staff. Also, Dr. Simon C. Moss, Professor of Physics, University of Houston, and Dr. Robert E. Green, Professor and Chairman of Materials Science Department, the Johns Hopkins University, have joined our group as consultants. Also, we have started experiments at NBS with Professor Haydn Chen, University of Illinois, Mr. Kee Chang Yoo, Brown University, Mr. Allan Goldman, State University of New York (Stony Brook) and Professor Ronald W. Armstrong, University of Maryland, as guest workers. We have established close relations with Professor Barton Roessler, Brown University, and Dean John Billelo, State University of New York (Stony Brook) to perform experiments at NSLS. Through the NSF international program, our group has established a cooperative program of materials science with CNRS in France, which aims at the collaboration of experiments using synchrotron radiation. This year as a start, we participated as a U.S. representative in a U.S.-France seminar on Applications of X-Ray Topography to Materials Science in Paris, France, and assisted in establishing a policy between the U.S. and French scientific activities in this area. We have been in close contact with Professor H. J. Queisser and Dr. W. Hartmann, Max-Planck Institut für Festkorperforschung, Stuttgart, Germany, on the development of real time imaging in x-ray topography.

We are now in possession of a 12 kw rotating anode x-ray generator. This will assist us to develop many preliminary experiments before they will be brought to NSLS and Cornell High Energy Synchrotron Source (CHESS).

Technical activities can be summarized as follows. More detailed descriptions of significant technical activities will be mentioned separately after this summary.

<u>Real Time Topography</u>: A portable and completely remote-controlled topographic system has been constructed, based on the concepts of asymmetric crystal topography[1] and x-ray magnifiers[2]. This prototype system was carried to the CHESS at Cornell University for a preliminary test. We obtained an extremely parallel (~ 1 arc/s) and wide (1.5 cm x 2.0 cm) monochromatic (8.0 keV) beam. This experiment requires alignment of as many as five perfect Si crystals and a sample crystal. Using this beam, we obtained a topograph from a single crystal of nickel with oxide deposits. Also, topographic images were recorded on a tape using an x-ray image intensifier video camera while the sample crystal was in motion. This provides a preliminary test for the real time capability of the system. Because of the extremely limited beam time available to us, the relationship between the brightness of the diffracted beam and the alignment of a collimating crystal has not been studied carefully. However, our trip to CHESS was quite successful, particularly considering the fact that this was the first wide beam multicrystal topography experiment using synchrotron radiation.

Specifications of a sample chamber for fracture experiments have been studied in collaboration with R. C. Dobbyn, Fracture and Deformation Division.

<u>Small Angle Scattering</u>: The specifications of beam characteristics and detector systems required for small angle scattering experiments for polymers, metals, and alloys have been studied in close collaboration with Drs. B. Dickens, F. A. Khoury, W. L. Wu, and G. T. Davis, Polymers Division. New concepts have been developed to improve the angular resolution (Δq) and the closeness of $q=o$. An experiment has just started using ordinary laboratory x-ray sources to prove the validity of this concept, as described in a separate abstract following this summary.

<u>Interface Spectroscopy</u>: A focusing tunable x-ray monochromator system has been constructed[3] for EXAFS experiments and fluorescence fine structure experiments. This will be the prototype mechanism for a synchrotron radiation beam line for measurements dealing with interface and surface

problems. Focusing elements and mini-detectors have been tested[4]. Design specifications for sample environmental chambers have been studied in collaboration with Dr. J. Kruger, Chemical Stability and Corrosion Division, for oxidation problems.

We are now establishing direct contact with material scientists at NRL in these three areas as well as in crystallography. Significant achievements have been made in the characterization of hardness testing in metals and the development of a new high-resolution x-ray diffractometer/spectrometer, as described in the following separate abstracts.

Reflection X-Ray Topography of Hardness Indentations in Copper and Nickel Single Crystals by K. C. Yoo, R. W. Armstrong, and M. Kuriyama

The plastic deformation zones surrounding microhardness indentations put into the (110) surfaces of relatively soft copper and nickel single crystals have been studied by the asymmetrical crystal topography (ACT) method. The method gives valuable information about the importance of workhardening to determining the level of the microhardness pressure and to determining the magnitude of its anisotropy for different directions of the indenter axes for Knoop or diamond pyramid indentations. This is demonstrated especially for copper crystals by the very pronounced appearance of the strain patterns for diffraction contrast obtained at either type of hardness impression. Both the cumulative dislocation displacements (for extinction contract) and their lattice rotations (for misorientation contrast) are employed in the analysis of the topographic strain patterns (see figure 1).

A New High-Resolution X-ray Diffractometer/Spectrometer Using Asymmetric Crystals by Haydn Chen and Masao Kuriyama

We have developed an x-ray diffraction system which is capable of producing and detecting x-rays with an angular resolution better than two seconds of arc. This system utilizes a pair of asymmetrically cut silicon single crystals in order to replace the conventional mechanical slits as well as a twocircle single crystal goniometer needed for necessary angular movements. These two crystals, having surface normals which deviate from the [111] direction by 13.5°, can be arranged either in an energy dispersive configuration (figure 2a) which yields a high-resolution (energy) spectrometer, or in a non-dispersive mode (figure 2b) which is ideal for high-resolution (momentum) wide angle/small angle diffraction work.

The diffraction principle responsible for this new development is the fact that the exit beam divergence coming from an asymmetrically cut crystal (ACC) is reduced from the rocking curve width of a symmetrically cut crystal (ω_s) as represented by the following formula

$$\Delta\Theta_{out} = \omega_s/\sqrt{m}$$

in which m ($=\sin\Theta_{out}/\sin\Theta_{in} = d_{out}/d_{in}$) is the magnification (or asymmetry) factor. Therefore, by using an ACC in its magnifying mode (i.e., $m > 1$),

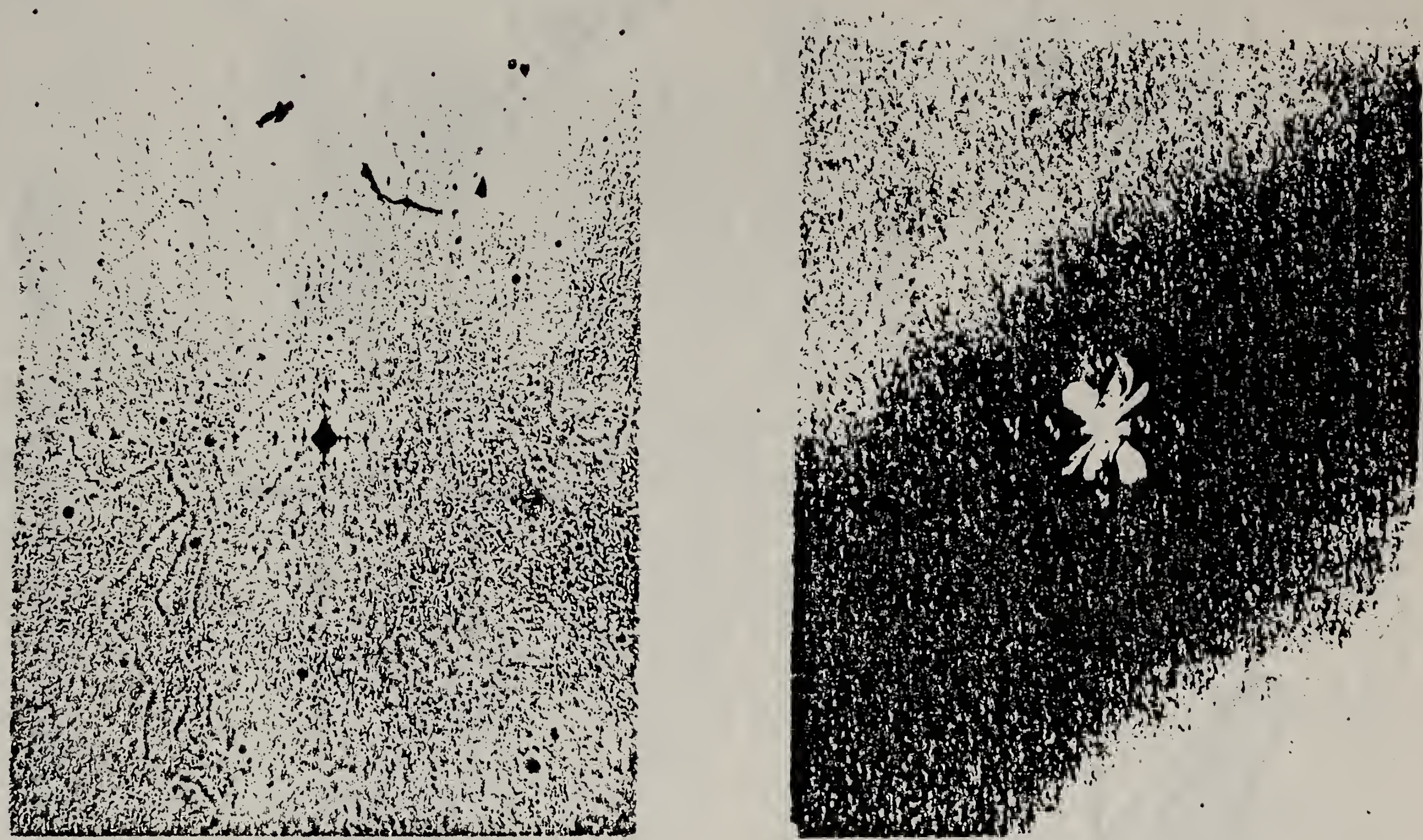

Figure 1. Magnified view (x50) of indentation markings on the (110) surface of a copper single crystal disk. The left view represents the ordinary optical microscope picture. The photograph on the right shows the strain distribution around those indentations observed by a special diffraction technique, called asymmetric crystal topography.

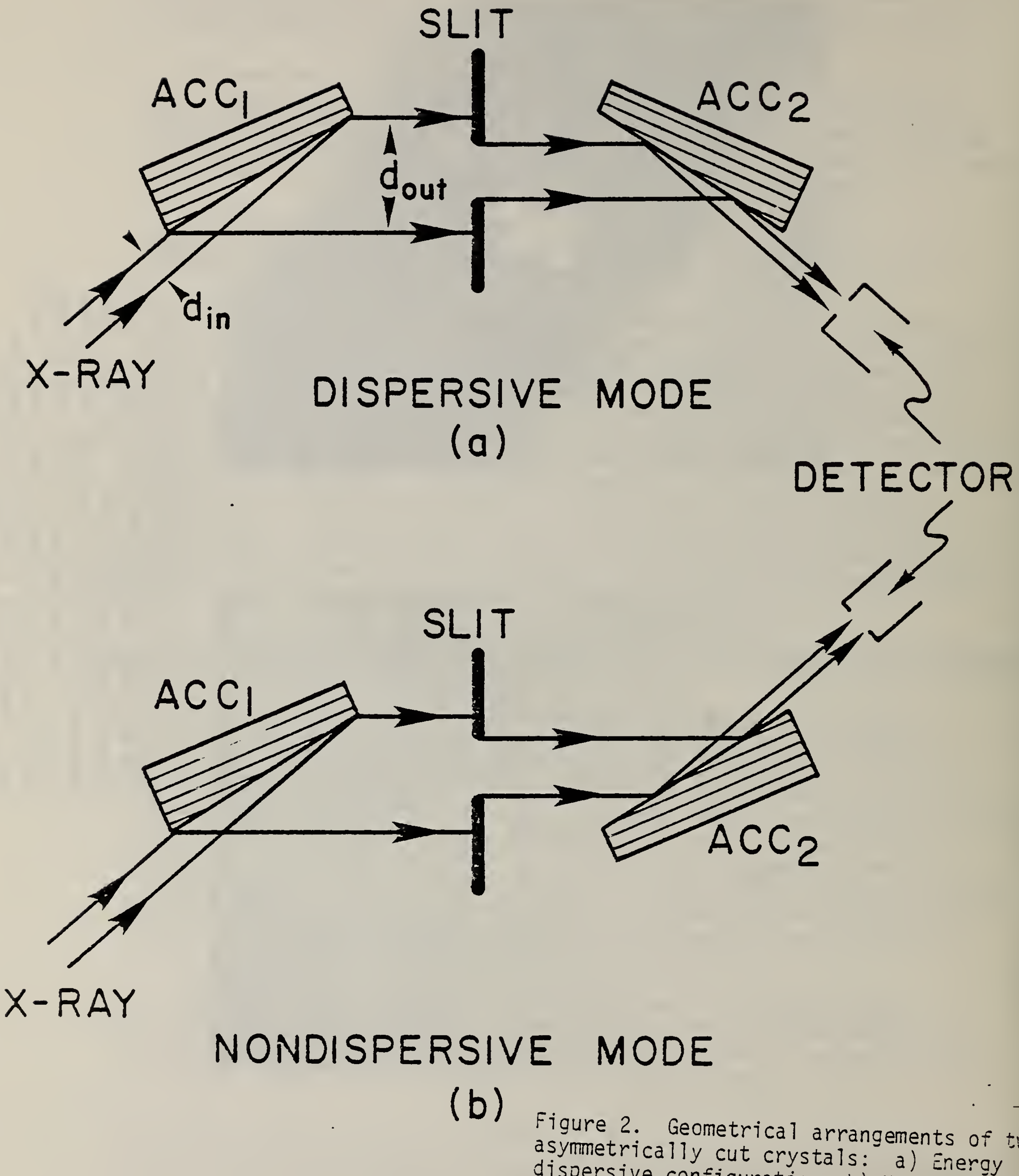

Figure 2. Geometrical arrangements of two asymmetrically cut crystals: a) Energy dispersive configuration; b) Nondispersive configuration. The second crystal is oriented in such a way that the incoming beam is accepted only within a very small angle.

we can, for a given wavelength, produce a parallel beam of x-rays with a theoretical angular divergence less than one sec of arc (e.g., ω_s = 6" for Si(111) reflection, with m = 38 and Cu Kα radiation, $\Delta\Theta_{out}$ = 0.97"). At the detector end, we use another ACC in its demagnifying mode (i.e., m < 1) such that a one second of arc acceptance angle is achieved. As a result, an extremely high-collimation x-ray facility is obtained.

When the system is used in its non-dispersive configuration (figure 2b), the measured line width diffracting off the second ACC under a perfect alignment conditon should correspond to the exit beam divergence from the first ACC or the acceptance angle of the second ACC, whichever is larger. We have measured this line width and a value of 2.8 seconds of arc (tilt) was obtained (figure 3). This observed value differs from the theoretical value of 0.97 sec of arc mainly because we were unable to manually adjust the goniometer arcs with sufficient precision. High precision rotations are possible using, for example, piezoelectric crystal tweakers and microstepping motors.

When a specimen is placed in between the two ACC's and the second ACC is rotated with respect to the specimen, a high-resolution diffractometer is obtained. A diffractometer of this type can be used for (elastic) small-angle scattering measurements. First, one has the angular resolution of 2 seconds of arc of scattering angle, regardless of a small spread of energy (e.g., Kα_1 and Kα_2), corresponding to $\Delta k = 8 \times 10^5$ A^1. Second, one also can make measurements <u>within the direct beam</u> at the extremely close vicinity of the direct beam direction (Θ=0°), without being hindered by the direct beam. This is possible, because the second ACC, acting as an ideal receiving slit, only receives photons coming within 2 seconds of arc of the desired scattering angle, even though the direct beam (Θ = 0°) strikes the second ACC completely. The smallest k (=$4\Pi\sin\Theta/\lambda$) that one can reach with this facility is 8×10^{-5} A^{-1} using Cu K radiation. This unique feature of defining a scattering angle regardless of photon energies enables one to circumvent the measurement difficulty associated with the blurring and overlapping effect in scattering patterns due to, say, individual polymer grains normally created by the finite (relatively large) size of mechanical slits in small angle scattering experiments. This system can also be used for wide-angle diffraction studies necessitating high angular resolution and the advantageous feature of parallel beams. Some examples in this category are residual stress measurements free of sample position effect, fine splitting of Bragg peak during phase transformation, thermal diffuse scattering in the vicinity of Bragg reflection, corrosion and oxidation on single crystal surfaces, etc.

One of the main concerns of this double crystal arrangement is the lack of photon flux. We, however, have measured the reflectivity of the second ACC with respect to the first ACC. A nearly perfect total reflectivity, better than 95 percent, was confirmed. This fact guarantees the highest flux consistent with the resolution obtained for the use of multiple ACC arrangements.

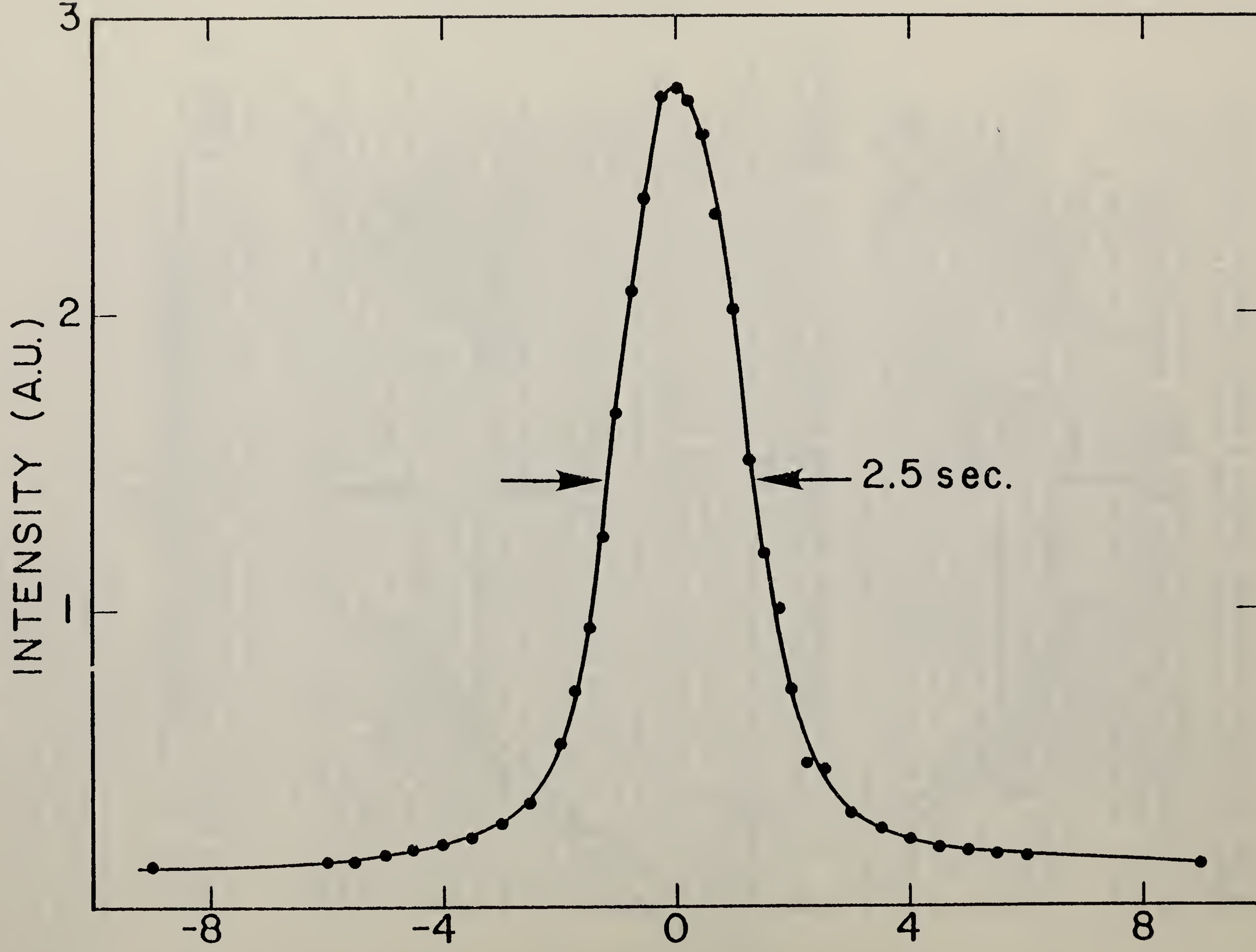

Figure 3. A spectrum obtained by the non-dispersive arrangement of two ACC's. The spectrum was obtained by rotating the second crystal only. This spectrum provides evidence that the second crystal acts as an ideal

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X-ray Residual Stress Evaluation in the Interior of Industrial Materials
Subtask 2 of Task 12142

M. Kuriyama, W. J. Boettinger, C. J. Bechtoldt

This project is part of the Metallurgy Division's participation in the NBS NDE Program. The objective is to develop a nondestructive method of mapping the distribution of residual stresses within industrial materials of considerable thickness. This has been carried out in collaboration with Robert Placious, Radiation Physics Division, Center for Radiation Research.

One of the nondestructive methods currently used for measurements of residual stresses in industrial materials involves the application of x-ray analysis for stress measurement. X-ray diffraction phenomena are used to determine macroscopic residual stresses in engineering components. The methodology of analysis and its basic principles are well known. Briefly, when materials are under stress, x-rays are diffracted with a Bragg angle which is slightly different from the Bragg angle expected in unstressed materials. The change in the Bragg angle is related to the alteration of atomic interplanar spacings when the crystal lattice of the materials is strained. As a measurement system, the essential part of this x-ray technique is the accurate measurement of lattice constants (or their changes) in materials by use of well-refined Bragg diffractometry. The surface residual stress can be evaluated from the strains measured by x-ray diffractometry using a set of assumptions regarding material elasticity and homogeneity. Although the accuracy obtained by this technique is, in principle, superior to any other method, an obvious shortcoming lies in its incapability of detecting strains (or stresses) in the interior of bulk materials.

Improved quality control of industrial materials and early detection of flaws in these components require quantitative information concerning the stress distribution near cracks and residual stress distributions after different types of cold working and heat treating or under various conditions of load. These demands naturally lead to the necessity of measuring residual strains in the interior of materials. Among many nondestructive techniques for the measurement of residual stresses, the x-ray diffraction technique, called Bragg diffractometry, excels in its accuracy. Yet this technique is incapable of detecting stresses in the interior of bulk materials. Last year we proved[1] that the desired resolution and detectability was possible if the energy dispersive diffraction method was employed with good x-ray optical conditions, using ordinary laboratory x-ray sources and thin materials. This year, we have used an industrial radiographic x-ray source with radiation up to 200 keV and commercial steel and aluminum plates up to 1 cm and 3 cm thick, respectively, to test if the methodology previously established is feasible outside the laboratory.

More than two years ago, we proposed[1] an entirely different approach to the x-ray evaluation of residual strains (or stresses) although it uses the principles of x-ray diffraction. This approach uses energy dispersive spectroscopy, where an energy dispersive solid state detector is employed within a well-collimated high energy beam of photons. Last year (NDE Annual Report 1979, p. 66) we proved[2] using ordinary laboratory x-ray sources and thin materials, that the desired resolution and detectability can be achieved for the determination of residual stresses if this technique is employed simultaneously with the curve fitting technique. The objective of this year's activity is to demonstrate this capability using an industrial radiographic x-ray source with radiation up to 200 keV and commercial steel and aluminum plates up to 1 cm (or a half inch) and 3 cm (or one and one-half inch) thick, respectively. If the feasibility of this technique is proved for use outside the laboratory, the mapping of a residual stress distribution inside an industrial material can be performed with relative ease on site.

To achieve this methodology, the following three major principles are involved:

(a) Well-defined diffraction energy peaks should be obtained at an energy range of about 100 keV. These high energy photons can penetrate through a quite thick material, so that the diffraction peaks obtained by these high energy photons guarantee to deliver the stress information within a bulk material.

(b) These diffraction energy peaks should have a Gaussian profile so that the curve fitting technique can be used for the determination of the centroid (or peak) positions.

(c) The measurement accuracy of lattice constants or their variations (hence, residual stresses) should be increased by a factor of 100, compared with the resolution limit of solid state detectors, by use of curve fitting. The relationship between the improvement factor (that is, the accuracy of determined strains) and counting statistics should be investigated.

All of these principles have been confirmed with thin materials using low energy photons. The use of high energy photons creates scattering problems and background problems which directly affect the accuracy of our measurements. We have succeeded in controlling these problems. The results are shown in the following.

(a) As shown in figure 1, diffraction energy peaks are clearly separated with significant intensities. This spectrum was obtained from a commercial steel plate (AISIC1015SAE1015) 3/8 inch thick. In this case, the scattering angle was set at $2\ \Theta = 5.7°$ with the incident divergence 3 m rad ($0.17° = 10$ min) and the receiving divergence much less than 3 m rad, so that the diffraction peaks can be obtained through the entire thickness of the sample at a given point of the sample surface. The spatial size of the beam on the sample is less than $1.5 \times 1.5\ mm^2$. The diffraction peaks are indexed as shown in figure 1. Note that the well-defined (211), (220), and (310) appears in the energy range between 90 kev and 150 kev in this transmission geometry. This result indicates that the previously mentioned principle (a) is completely satisfied.

(b) Figure 2 shows an example of the observed spectral profile, say (110), which has been fitted by a Gaussian curve with a linear background. A perfect Gaussian fitting demonstrated here certainly indicates a great promise in the precision determination of centroid (or peak) positions for each observed energy peak. Hence, principle (b) has also been confirmed experimentally for high energy photons.

(c) We are now in the process of proving principle (c). And further, efforts are being made to increase the scattering angle without loss of resultant intensities in peaks, so that one can really determine stresses within small volumes inside materials.

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Acoustic Emission for NDE
Subtask 3 of Task 12142

J. A. Simmons, R. B. Clough

Acoustic emission (AE) is a relatively new nondestructive testing technique relying on the detection of stress waves emitted during the motion of flaws or from other microstructural changes in a highly stressed region of a structure. This technique has been applied to aerospace, petrochemical, bridge, and power plant structures to monitor structural integrity. It has also been used to detect faulty welds in production lines. In addition, AE has been used for materials research studies on microstructure related properties such as deformation mechanisms, phase transformations, and fracture.

Highlights in the AE area in the Metallurgy Division during the past year are (1) development of indentation techniques for the experimental production of AE signals from material defects; (2) experiment design for

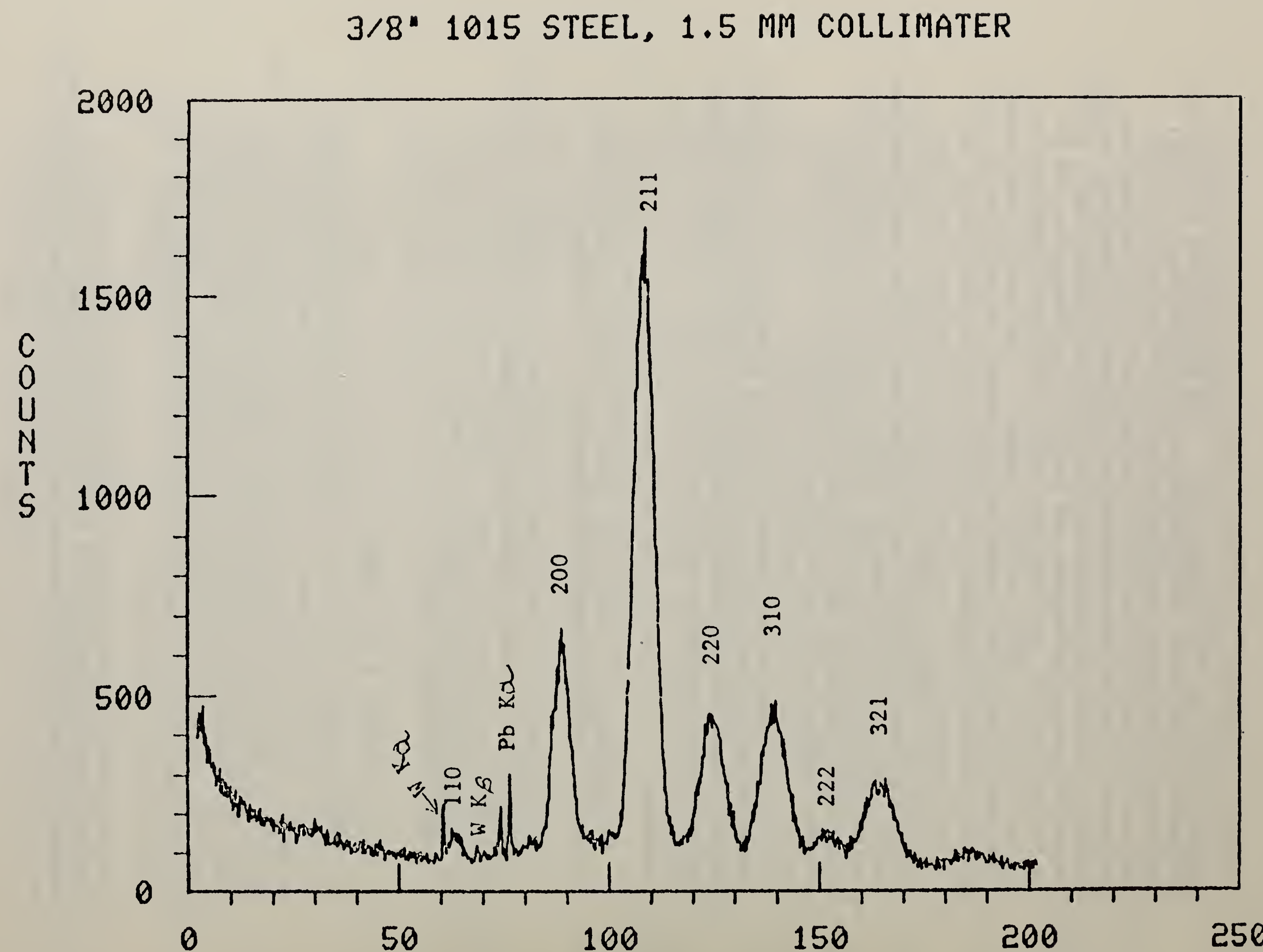


Figure 1. A Bragg diffraction energy spectrum obtained from a commercial AISI-C1015-SAE1015 steel plate 3/8 inch thick. The scattering angle is 5.7° ensuring a transmission geometry through

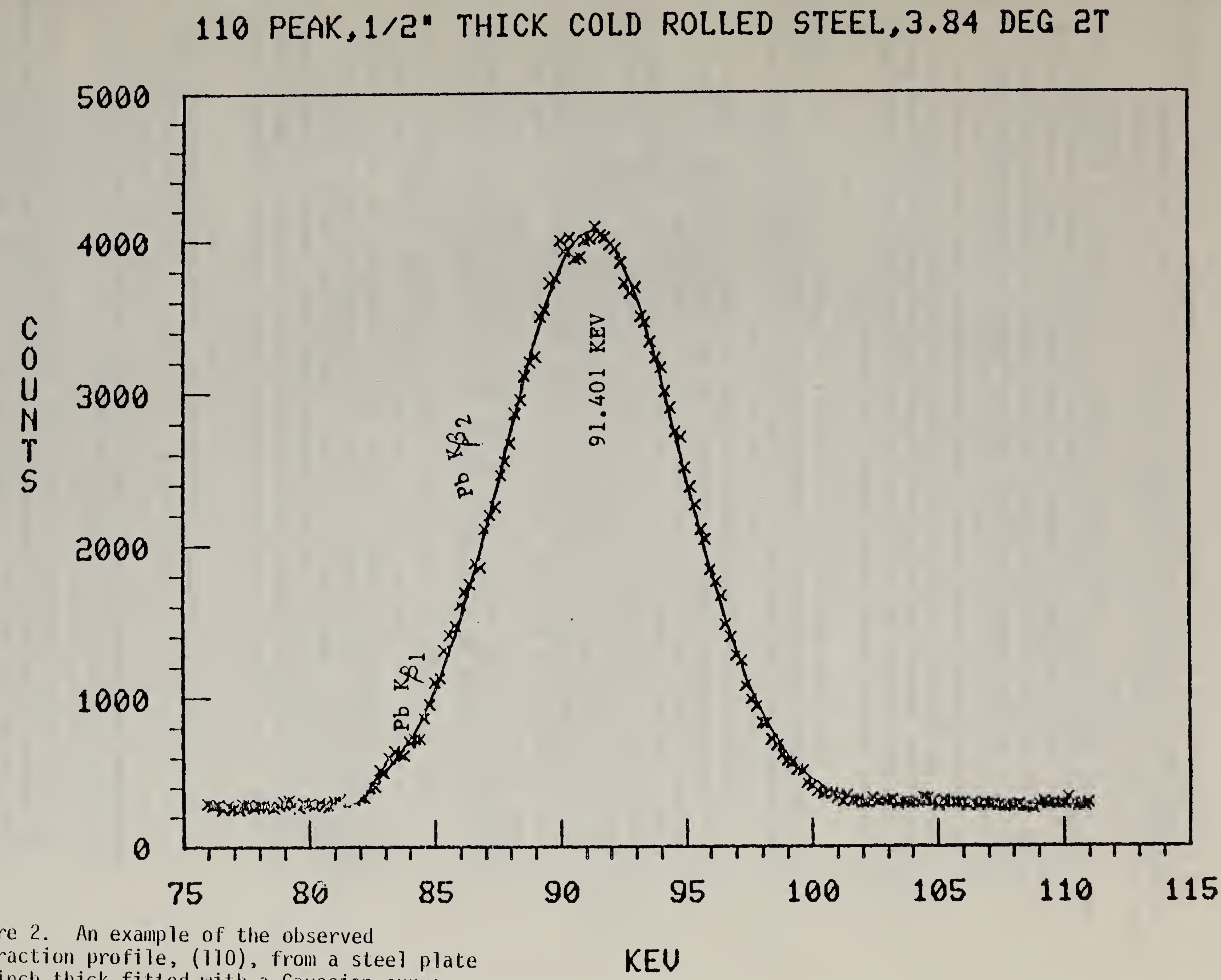


Figure 2. An example of the observed diffraction profile, (110), from a steel plate 1/2 inch thick fitted with a Gaussian curve with linear background.

multichannel AE source characterization; (3) progress on acoustic emission theory and signal processing techniques; and (4) guest workers and interlaboratory collaboration with AERE, Harwell.

(1) Indentation techniques have been highly developed for use with ceramics materials for studying crack growth under controlled loading. We have therefore begun to adapt the technique to use with metals as a new type of controllable acoustic emission source. Besides the control possible on the growth of defects, this method also ensures that the source location is fixed, an essential feature for AE signal analysis and microstructure correlation. Such a technique provides, under the proper conditions, a means of generating reproducible AE signals from known types of sources having predictable signatures. This allows one to actively control AE and thus constitutes an advance in the technique from its present mode of merely passive listening.

We have been developing the indentation method in metals and alloys so far using three new types of methods: (a) indentation brittle fracture; (b) indentation fatigue; and (c) indentation stress corrosion cracking.

The brittle fracture method has been successful on steels which have been hardened by heat treatment. It has been found that if the surface is hardened to greater than 45 ± 5 on the Rockwell C scale, indentation by a diamond pyramid will produce subsurface penny-shaped median plane cracks generally less than a millometer in size. By controlled loading it is possible to produce identical repetitive signatures, typically on the order of 10 but sometimes over 100. Comparison with SEM micrographs suggests that these signals are produced by incremental crack growth along carbides and martensitic platelets. This idea has been exploited in the design of a portable "acoustic embrittlement detector" which can detect locally embrittled areas of structures such as in the heat affected zones of welds or on critically stressed areas.

This technique has also been studied as a means of producing localized fatigue cracks in 2024 and 7075 aluminum where, after sufficient load cycling, reproducible signals are emitted. Comparison of AE signals and SEM micrographs shows characteristic differences in signals in these alloys which are explainable in terms of the defect microstructure. Finally, fatigue cracks can be generated and after removal of the indentor a drop of corrosive medium is placed over the indentation. The residual stress is sufficient to generate numerous stress corrosion signals which are also being studied in relation to microstructure.

Interactive experiments with Dr. Wadley of AERE, Harwell, have also begun using a plate indented with a bias stress to give further control on the defect morphology. There are in fact a number of interesting experiments suggested by this newly available research tool which cannot be summarized now but appear quite fruitful.

(2) A high speed interface has been designed and is being constructed for monitoring up to 16 AE channels using 20 MHA transient A to D recorders with variable timescale for synchronization, up to 100 dB dynamic range, and less than 100 millisecond dead time to dump all channels. This

interface will be connected to our new microcomputer and will be operated remotely in the laboratory under computer control. Monitoring of experimental parameters will also be under computer control. A loading machine capable of producing bias stresses in large metal plates is being designed to permit creating defects under variable but controlled conditions. This instrumentation will permit us to simultaneously monitor at several transducer sites AE from defect sources produced on a plate by indentation or other directed energy loading. Using the theory developed at NBS we will then be able to calculate the stress drop history characterizing the source. Knowledge of the stress drop history gives information on the defect orientation and geometry, then dynamics of the emission process, and the local stress conditions. This information will be used interactively with metallurgical examination and defect mechanism modeling to enhance our understanding of defect dynamics and to develop critical AE indicators to signal critical feature events.

(3) The theory of acoustic emission from defect sources has been extended to include inhomogeneities such as martensitic transformations and microcracks. In addition, an extensive series of computations of waveforms to be expected in steel and glass plates have been carried out. These calculations have graphically demonstrated the great directionality of acoustic emission signals as well as pointing the potential new signal processing techniques. The plute code is currently under revision to allow more accurate Fourier transforms of the plate solutions to be computed, thus permitting more reliable inversion methods. Finally, the theory of noise propagation has been carefully studied using quadroutic noise statistics and criteria have been developed for optimal noise filtering to use in conjunction with deconvolution techniques.

(4) Dr. M. Rosen of Technion, Israel, will be with us for the near future, opening a new series of AE studies. Dr. Rosen's knowledge of materials science will add considerable breadth to our program and will provide additional opportunities to make use of the quantitative AE techniques we are developing.

Dr. Haydn Wadley of AERE, Harwell, has also joined the Metallurgy Division as a guest worker for one year with the Structure Characterization Group. He will work primarily on acoustic emission studies of materials in our Division. Dr. Wadley is well known in the acoustic emission community for his innovative experimental studies of materials by quantitative acoustic emission.

Dr. Wadley is joined with Dr. James E. Sinclair of Harwell for three months who will be helping to implement the plate theory in AE signal analysis.

These visits have resulted from informal cooperation between the Harwell group and the NDE program at NBS. Both groups are working on the development of a new type of acoustic emission methodology which will permit reconstruction of the emission source. To achieve this, a series of critical experiments will be performed using the combined expertise of both groups. If successful, the new multichannel method will provide information unobtainable by other known methods on crack growth, metallurgical phase changes, and other dynamic materials effects. Besides basic materials studies, the method has great potential for quality control in industrial processes such as welding and for in-service surveillance of aircraft structures and nuclear pressure vessels.

The first phase of the NBS/EPRI AE program has been completed and an extensive two volume report has been submitted. ASTM interaction continues strongly with the Vice-Chairman of ASTM Subcommittee E7.04 coming from this Division.

There has been substantial interaction with the NDE community, particularly in the nuclear industry, with one of our members having been Session Chairman, a member of the Organizing Committee, and who now has been selected to be the General Chairman of the Fifth International Conference on NDE in the Nuclear Industry, to be held in 1982 and sponsored by ASM, ASNT, and ANS.

Ultrasonic Materials Characterization
Subtask 4 of Task 12142

R. Mehrabian, S. Fick, R. B. Clough, J. A. Simmons

This is a new activity using ultrasonic techniques for nondestructively measuring microstructural material parameters. Ultrasonics as commonly used in pulse echo or imaging systems detects macroscopic discontinuities such as flaws or interfaces in material structures. However, the measurement of ultrasonic attenuation and velocity changes or the study of the absorption and transmission spectra of scattered ultrasonic waves provides a wealth of detail on the mean microstructural properties of metallic materials. These techniques have great potential for measuring texture, porosity, and multiphase distributions, as well as for studying the kinetics of phase transformations both by observing and inducing such transformations.

Work in cooperation with Prof. R. Green of Johns Hopkins University has been initiated on ultrasonic characterization for "soft spots" in aluminum alloys. Detailed description of the overall program in this area is given under subtask 3 of Task 12145. The first priority of the effort in this task is to develop a reliable alternate NDE method for detection of these "soft spots." Velocity, attenuation, and ultrasonic scattering techniques are being employed and their reliability assessed. Longer-term studies are contemplated of the kinetics of the aging process itself leading to better specifications for such alloys in the future.

Currently, the relative merits of various developmental techniques for measuring ultrasonic attenuation and velocity are being experimentally investigated. Since ultrasonic parameters are extremely sensitive to measurement techniques, considerable effort has been devoted to the optimization of procedural and equipment design. Methodologies under investigation include the use of test fixtures incorporating design features allowing transducer-to-specimen alignment independent of dimensional variations in the specimen. Test fixtures employing long path and direct transducer-to-specimen contact in liquid coupling media have been designed and constructed. Transducers capable of high efficiency operation at the high frequencies necessary for adequate sensitivity to precipitate development in a selected alloy have been designed and fabricated. The use of conventional transducer designs at higher than normal frequencies has also been investigated. Results obtained thus far indicate that further developmental effort is necessary and justified. Longer-term studies are contemplated of the kinetics of the aging process itself leading to better specifications for such alloys in the future.

Doppler-Broadened Positron Annihilation Lineshape for Detection of Defects in Materials
Subtask 5 of Task 12142

R. C. Reno, L. J. Swartzendruber

Positrons that annihilate in a metal produce gamma rays whose energy distributions can be explained in terms of a Doppler shift caused by motion of electrons. When defects are present in the metal, they attract and trap positrons, and alter the Doppler shifts. A measurement of doppler-broadened annihilation lineshapes thus gives information on the defect nature of materials. Both the annihilation process and the method of detection leave the sample intact, so the technique is extremely useful for the nondestructive evaluation of materials.

Doppler-broadened lineshape measurements are performed by placing a positron source in contact with the sample to be studied (see figure 1). Positrons enter the sample, slow down to thermal energies, and then annihiliate with electrons. Each annihilation produces two gamma rays with a total energy equal to the rest mass energy of the positron-electron pair (1022 keV). The distribution of energy between the two gamma rays depends upon the electronic and defect structure of the sample, and is measured with a high resolution solid state detector-multichannel analyser system. A lineshape parameter, S, is defined which is a measure of the inverse width of the distribution.

The addition of a small number of defects to a metal will cause a significant change in the lineshape parameter, and it is this sensitivity that is used to observe changes in defect concentration and type. We have used this technique to study defects in cold worked titanium and, more recently, have begun to study precipitation hardening in aluminum alloys. In the latter study, some results of which are shown in figure 2, we observe significant changes in S parameter as microprecipiates form during aging.

Magnetic Measurements
Subtask 6 of Task 12142

L. Swartzendruber

One of the most extensively used techniques in magnetic NDE is the magnetic particle method. The application of this method is currently guided by empirical rules for the amount of magnetization required to

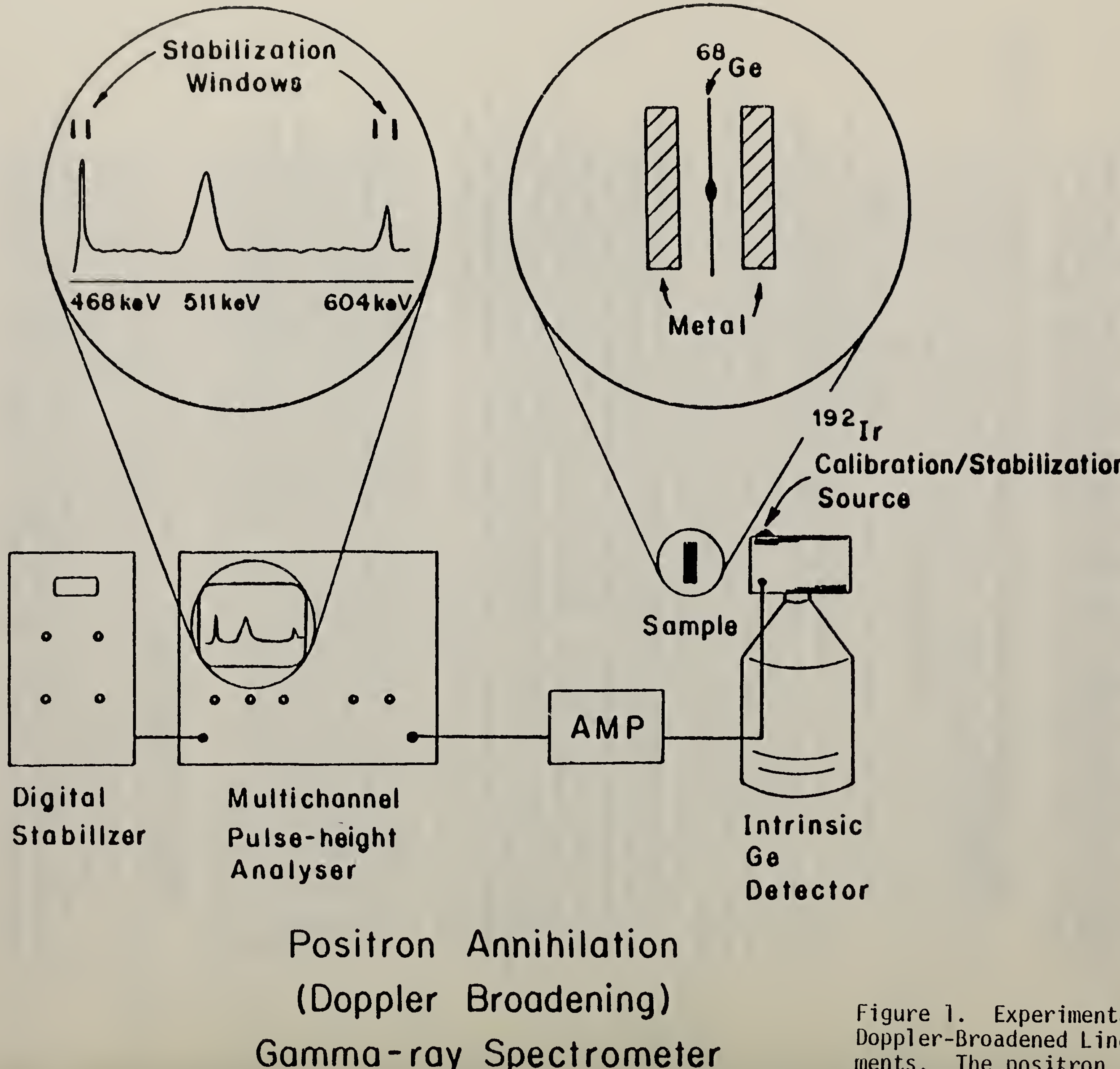


Figure 1. Experimental Apparatus for Doppler-Broadened Lineshape Measurements. The positron source is 25 microcuries of ^{68}Ge. An ^{192}Ir source is used to calibrate the energy scale and maintain system stability.

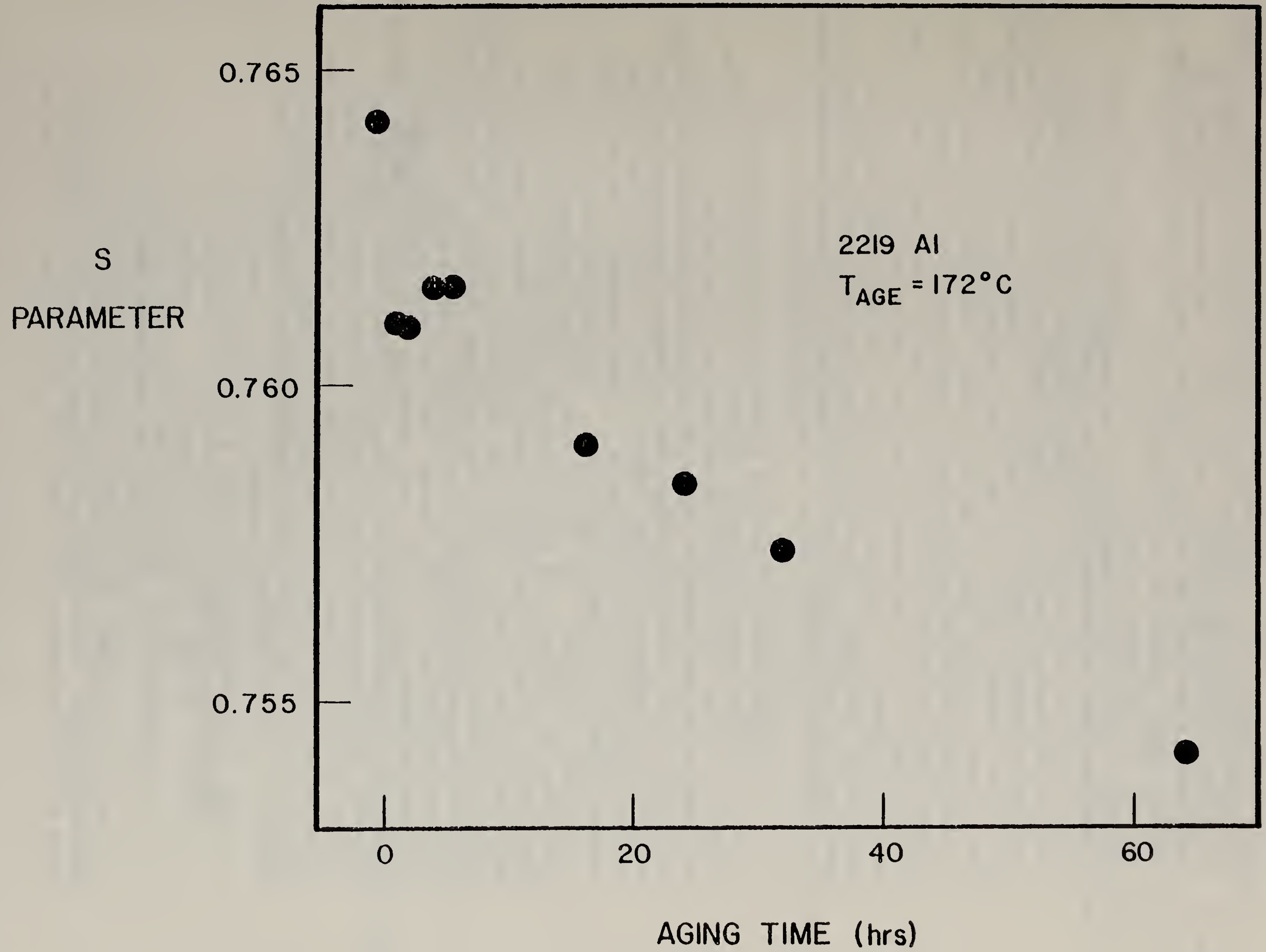


Figure 2. S Parameter Data for a 2219 Aluminum Alloy at Various Stages of Ageing.

achieve the desired results. Also, there is no acceptable method for independently testing magnetic inks. The first steps in placing magnetic particle inspection on a more quantitative and reproducible basis are an understanding of how the leakage field from a defect is influenced by the defect geometry and level of magnetization reached by the material, and a detailed description of the influence of the leakage field on the formation of an indication by the magentic ink.

We have previously investigated the leakage fields from a steel ring with artificial defects introduced by drilling a series of small holes at varying depths below the sample surface. The ring geometry used was the same as specified in MIL-E-6868E and in the new ASTM recommended practice for magnetic particle inspection. It was found that all residual and active leakage fields could be closely approximated using a linear dipole model provided that an apparent depth, less than the actual depth of the defect below the surface, and an equivalent dipole strength, greater than that predicted by the linear theory, were used. One of the disadvantages of the ring geometry was that the magnetization level actually achieved in the steel ring varied with the defect depth and could not be monitored. It was also found that the artificial defects specified for the ring were too close together in that the leakage field from one defect was distorted by its neighboring defects.

To overcome these difficulties a sample containing artificial defects with the geometry shown in figure 1 was constructed. Using the pickup coil shown, the level of magnetization in the material can be monitored while the leakage fields from the artificial defects are being measured. A Hall effect probe was used to measure the tangential and perpendicular components of the leakage field at five different points on the hysterisis curve of the sample. These leakage fields were least squares fitted to a linear dipole model. Typical data and fits are illustrated in figure 2. As for the case of the ring geometry, it was found that the residual and active leakage fields could be closely approximated using a linear dipole model with an apparent depth and an equivalent dipole strength. Both the equivalent depths and the equivalent dipole strengths were roughly the same as those found for the tool steel ring. An interesting feature of the results on the sample of figure 1 is that the magnitude of the leakage field increases almost linearly with the applied magnetic field even after the material is driven into saturation. Further studies are planned on other defect geometries including very narrow cracks and slots of various depths in a sample similar to that of figure 1. Using these results it should be possible to devise more valid tests for the quality of magnetic inks and to specify more precisely the level of magnetization required to detect defects of a given geometry.

Eddy Current Standards
Subtask 7 of Task 12142

L. H. Bennett, J. R. Cuthill, L. J. Swartzendruber

The specifications for a set of aluminum conductivity standards were established. Four alloys were chosen to cover the conductivity range of 30 to 60 percent IACS; 2024-T351 for a standard with nominal

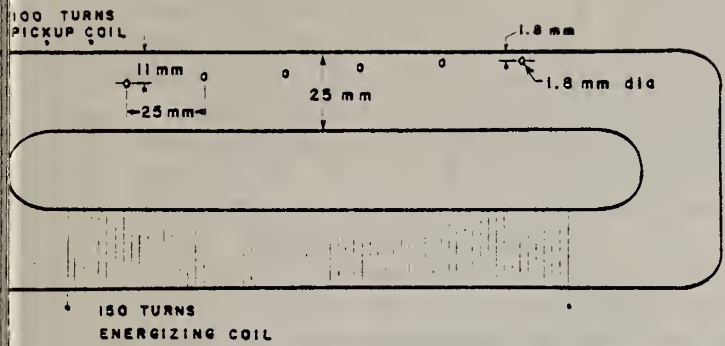


Figure 1. Test yoke used for measuring leakage fields from artificial defects. The entire yoke is 25 mn wide. The artificial defects are six holes drilled as shown. The material is a low carbon steel. A 150 turn coil is used to magnetize the yoke and a 100 turn pickup coil is used to determine the magnetization level reached inside the yoke.

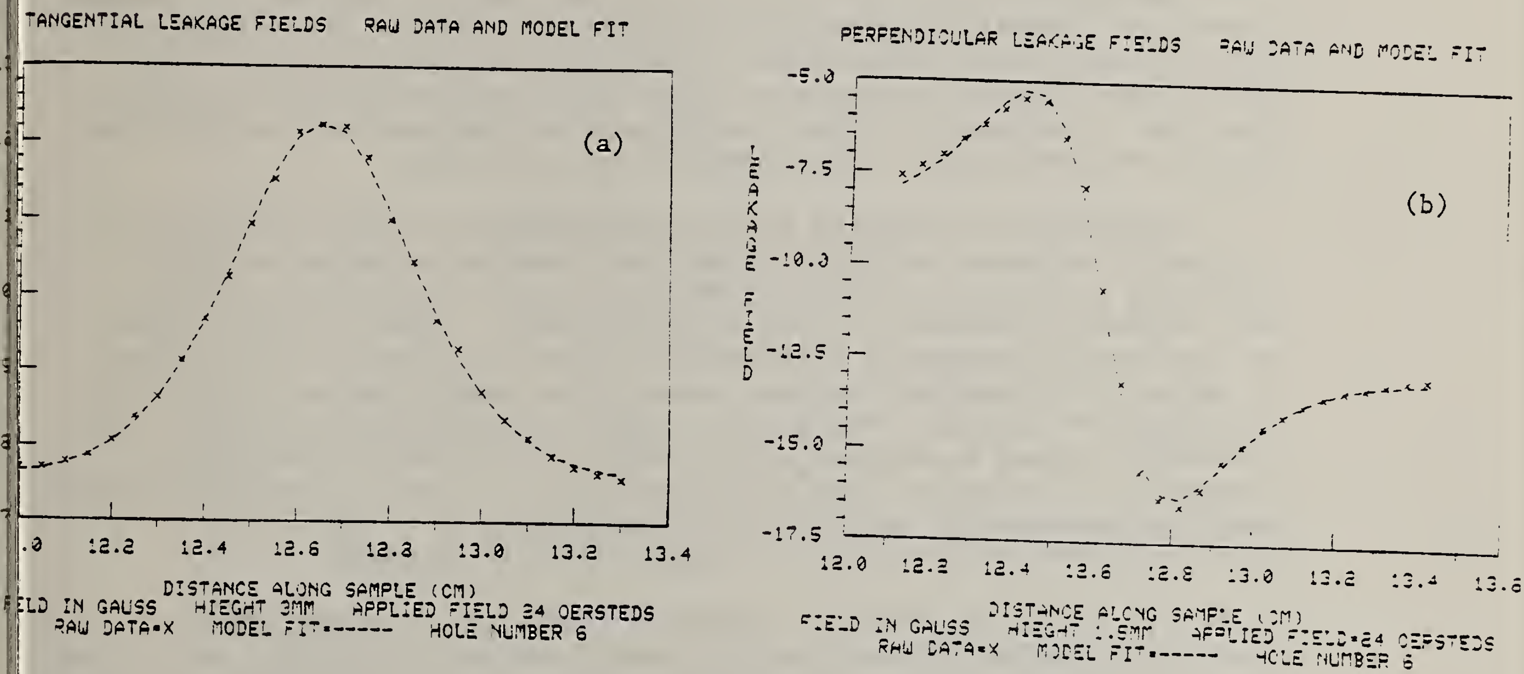


Figure 2. Leakage fields measured from the yoke shown in Figure 1 compared with the field calculated from a magnetic dipole model. (a) Tangential field with an applied field of 24 oersteds. (b) Perpendicular field with an applied field of 24 oersteds. The crosses are data points and the dashed line is a least squares fit to a linear dipole model.

conductivity of 30 percent IACS, 6061-T6 for a standard with nominal conductivity 40 percent IACS, 2024-0 for a standard with nominal conductivity 50 percent IACS, and 1100-F for a standard with a nominal conductivity of 60 percent IACS. These alloys are to be milled into coupons 44.5mm x 44.5 mm x 9.5 mm from a plate 12.7 mm thick. The surface finish on both sides is specified to be better than 1 μm RMS and each alloy is to be anodized in a distinctive color. A set of 100 of each of these standards has been ordered and received and turned over to the Electrical Measurements and Standards Division for calibration. Work has been initiated on finding a suitable alloy and specifications to cover conductivity standards in the range of 1 percent IACS which are required for use with titanium alloys, and to determine what standards would be desirable for use with eddy current measurements on steel.

Scanning Electron Microscope
Subtask 8 of Task 12142

D. B. Ballard

The NML-SEM facility consisting of two scanning electron microscopes (SEM) and associated equipment have provided over 1,200 hours support to other research activities at NBS. Two approaches are used; one is the particular scientist operates the SEM in the examination of his samples. The other arrangement is that the SEM services and analyses are provided by the SEM laboratory. Some examples are as follows.

Discovery by an outside aircraft manufacturer of very low tensile strength aluminum alloy thick plate stock produced by Reynolds Metals initiated a request by NASA that NBS review the relationships between NDE, mechanical properties, and microstructures. Detailed description of the overall program in this area is given in subtask 3 of Task 12145. A series of SEM photomicrographs taken in the magnification range of 50 to 5,000 X of sections from as-cast ingots and subsequent different heat treatments showed macrosegregation, recrystallization, grain growth, formation of inclusions, and precipitation of "Θ" phase. This information was complemented with optical and TEM microscopy to illustrate the effect of fabrication process variables on microstructure.

Part of the Recycled Oil Program includes the characterization analysis of mechanical wear tests. Twenty-one sets of 52100 steel ring-and-block combinations tested at different loads with different ASTM lubricants have been examined with the SEM for wear scar surface topography. Studies of entrance, center, and exit areas are being correlated with data of friction and temperature data in an effort to develop understanding of wear mechanisms involved. The goal is to develop a data base of wear observations on mechanical parts for evaluation of lubrication systems using rerefined oil.

Work on three different SRM's concerned with the SEM was conducted. One was the production of 150 units of Resolution Test Sample SRM-469, formerly designated RM-100 Aluminum-Tungsten dendrites. This sample is one of four available; however, it can be used from magnifications of

2,000 X to 100,000 X. The second activity was the accurate measurement of four crack widths that varied from 0.2 to 2μ on a prototype SRM to be issued for the evaluation and calibration of crack detection using the NDE method of liquid penetrant or visual optical techniques. This measurement technique was made possible by use of SRM-484 (Magnification Calibration of Sample for the SEM). The number of SRM-484 units sold to date is 346. An additional 100 units have been calibrated and will be available for issue. Thus far it is the only sample that has traceability to NBS national standards.

Draft #5 of the "Standard Practice for Calibrating the Magnification of an SEM Using NBS-SRM-484" has been approved by E-4 of the ASTM. Final approval by the ASTM Society is expected in 1981.

METALLURGICAL PROCESSING FOR ALLOY DURABILITY
Task 12143

Metals processing research plays a central role in the Division's activities and is the controlling factor in the interplay between the other three tasks. The properties of alloys depend on their compositions and microstructures, which are dictated by their processing history. Thus, the effective performance of components in societal use depends strongly on solidification and solid state transformation processes, diffusion, and other kinetic changes that alloys undergo during production and shape forming operations. The central objective of this task is to develop data, measurement techniques, theory, and predictive models relating variables during metallurgical processing to microstructures, hence properties and performance of alloys. In addition, the Diffusion in Metals Data Center of the National Bureau of Standards is located in this group. This Center is a national metallurgical resource that provides a central source of extensive evaluated data on diffusion to the technical community at large.

As part of the new emphasis on materials processing technology in the Center for Materials Science, projects have recently been initiated on rapid solidification and on the kinetics of grain boundary diffusion and migration. Guidelines for producing more homogeneous alloys and rules governing the formation of non-equilibrium alloy compositions, metastable crystalline phases and metallic glass structures are being developed by application of solidification theory to rapid solidification conditions. Surface modifications introduced by diffusion-induced grain boundary migration and by electron beam melting of surfaces with subsequent rapid solidification are being investigated.

The emphasis in this work is on development of predictive techniques, based on quantitative measurement and testing of predictive models. For example, calculations which include surface tension effects and deviations from equilibrium at the solid-liquid interface show that in many alloys plane front solidification will be obtained not only at slow solidification velocities but also when sufficiently <u>fast</u> cooling rates are applied. At these rates the usual dendritic microstructure will disappear and much improved alloy homogeneity can be obtained. As a second example, an apparatus especially designed to provide rapid controlled directional solidification was used to show that metallic glasses are formed in Pd-Si-Cu eutectic alloys when the solidification velocity is greater than 0.2 cm/s. This result is consistent with theories which emphasize the importance of eutectic crystallization rate rather than nucleation rate in controlling metallic glass formation.

Significant success also was achieved in measuring convection effects during directional solidification, in providing improved methods of measuring liquid-vapor surface tension, and in developing ultrasonic techniques for real-time measurement of solidification velocity. Changes in alloy segregation resulting from solutal convection were used to estimate the decrease in convection from applying magnetic fields during solidification and by solidifying downward (liquid below solid). Experimental results in Pb-Sn off-eutectic alloys showed that magnetic fields up to 0.1 T had no measurable effect on alloy segregation arising from convection but downward solidification greatly reduced this segregation. Tests with a pulse-echo ultrasonic system on tin specimens show that alloy solidification velocities up to at least 4 mm/min can be accurately measured from either the solid or liquid side of the interface.

Diffusion-induced grain boundary migration is an unexpected new phenomenon that produces greatly enhanced diffusion at low temperatures. In recent experiments done as part of this task, appreciable alloying of copper by zinc was found to occur at temperatures which are much too low to allow measurable lattice diffusion. Since grain boundaries provide easy diffusion paths, zinc atoms in these experiments are presumed to enter the copper specimens by diffusion along grain boundaries. In order to accommodate these additional atoms, the grain boundaries then migrate and leave behind a zinc-alloyed region. Eventually the grain boundaries can migrate across entire grains, thus producing in effect a large increase in volume diffusion. This effect can yield significant alloying or surface degradation at surprisingly low temperatures. An intriguing aspect of this process is that a small amount of actual lattice diffusion apparently will prevent the effect from occurring.

In diffusion data work, compilations were prepared and evaluations were made of kinetic parameters involving diffusion and reaction rates in metal hydrides, proposed for use as hydrogen storage materials, and of mass transport data in copper alloys and stainless steels. In order to handle the diffusion data information efficiently, an effort has been undertaken to computerize the classification and bibliographic data for documents in the Diffusion in Metals Data Center.

Task members were active in organizing a major international conference on Rapid Solidification Processing: Principles and Technologies held in March 1980 and co-sponsored by Department of Defense agencies and NBS. Also, task members serve on advisory committees for the Solar Energy Research Institute and the National Aeronautics and Space Administration; on boards of international journals on diffusion and crystal growth; and on working committees of the ASTM, AIME, American Society for Metals, and the National Materials Advisory Board.

Rapid Solidification
Subtask 1 of Task 12143

W. J. Boettinger, S. R. Coriell, R. J. Schaefer, J. W. Cahn

This project is focused on an increased knowledge of the kinetic processes which occur during the rapid solidification of alloys. A broad class of experimental results on rapidly solidified materials are difficult to understand because existing theory needs extension to higher solidification velocities and because accurate quantative experiments are difficult to perform due to the high cooling rates and small specimen sizes. This project is currently directed toward three areas: (a) microsegregation as influenced by the shape stability of the freezing interface, (b) thermodynamics, and (c) glass formation by rapid cooling of eutectic alloys. In these areas, new theoretical predictions are being examined experimentally but also experiments are being performed to direct theoretical efforts in proper directions. Brief summaries of progress in these areas are reported below.

Microsegregation and Stability at the Solidification Interface: The phenomenon of solid-liquid interface stability during directional solidification of a binary alloy was reexamined with special emphasis on very rapid solidification rates ["Interface Stability During Rapid Solidification," S. R. Coriell and R. F. Sekerka, Rapid Solidification Processing: Principles and Technologies, Volume 2]. For ordinary solidification rates, the predictions of the perturbation theory of morphological stability lead to results that are similar to those implied by constitutional supercooling; however, at very rapid solidification rates, the perturbation theory predicts a vast increase in stabilization in comparison to constitutional supercooling. There appear to be two dominant effects. The first effect can occur even if there is local equilibrium at the solid-liquid interface; it is known as absolute stability and arises because only short wavelength perturbations are important at high velocities and these are stabilized by surface energy. Numerical calculations for aluminum with various concentrations of copper and a liquid temperature gradient of 2 (10^4) K/m show that absolute stability is important for solidification velocities above about 0.01 m/s; in fact, for copper concentrations less than 6×10^{-3} wt. percent, the interface is stable at any solidification rate. The second effect is caused by departure from local equilibrium at the solid-liquid interface. Although the exact forms of such departures, let alone their magnitude, are not well known, the perturbation theory can be modified to include their salient features. Most departures from local equilibrium lead to increased stability. For example, all constitutional effects will vanish as the distribution coefficient approaches unity. Finally, other factors were examined with an aim toward the identification of a realm where experimental test of the theory would be meaningful, e.g., solidification of a thin liquid layer and growth into supercooled melts.

Experimental study of morphological stability during rapid solidification has been initiated, using dilute alloys of silver in aluminum. In this system the concentration at which instability is predicted to start falls within a range which is useful for experiments (0.1 to 1 percent Ag). At these compositions, instability can occur at solidification velocities greater than a critical value which is typically about 10^{-4} to 10^{-3} cm/sec, or less than a second critical value which is typically about 1 to 10 cm/sec. The objective of the experiments is to measure the stability to instability transition at the higher velocities, which are not attainable by conventional unidirectional solidification methods and which will therefore be achieved by electron beam surface melting.

Preliminary experiments in which the electron beam was scanned across the surface of aluminum and stainless steel samples demonstrated the need for improved control and stability of the electron beam, and these improvements are now nearing completion. In the experiments as carried out on the upgraded apparatus, the electron beam will be rastered very rapidly over a small area of the metal surface to produce effectively uniform surface heating with one-dimensional heat flow within this area. Calculations comparing heating by repetitive pulses to heating by a continuous source have been carried out to determine the rastering frequency required to simulate the continuous heat source. Solidification velocities are computed from a one-dimensional heat flow model. The desired velocities are obtained by the use of heating times ranging from 4×10^{-3} sec to 10^{-1} sec and power densities from 5×10^7 to 5×10^8 W/m^2.

Thermodynamics: One of the current approaches to treating deviations from local equilibrium (interface kinetics) during solidification is to presume that while local equilibrium is not established at the liquid-solid interface, it is established within each phase itself. This permits the use of thermodynamic free energies of individual phases to draw conclusions that restrict the realm of possible processes that occur during rapid solidification. In a recently submitted paper ["Rapid Solidification", J. W. Cahn, S. R. Coriell, and W. J. Boettinger, Proceedings of Symposium on Laser and Electron Beam Processing of Materials, Materials Research Society] such an analysis was used to place a bound on the maximum extended solubility possible by rapid solidification for systems with retrograde solidi. Predictions of this analysis are consistent with experiments at other laboratories on the maximum solubilities of dopants in laser melted Si. Other work in this area concerns metastable reaction sequences and is presented in a recently submitted paper ["Thermodynamics of Metastable Equilibria," J. W. Cahn, Rapid Solidification Processing: Principles and Technologies, Volume 2]. Thermodynamic principles rank phase equilibria but not phases in a hierarchy of increasing stability. Thermodynamics imposes precursor rules in multicomponent systems in which a prior reaction is required before a phase can appear. A given hierarchy persists over a domain on the phase diagram bounded by surfaces on which the ranking of two equilibria changes. Multicomponent phases per se do not form a hierarchy because a given phase can disappear and reappear in a sequence of spontaneous processes. Processing for producing metastable phases must place the system within a domain in which the desired phases can form spontaneously from the available phases.

Glass Formation by Rapid Cooling of Eutectic Alloys: The relationship between eutectic solidification and the ease of formation of metallic glasses is being investigated. For many systems, crystallization, including partitionless crystallization, of alloys into a single phase solid is impossible over a wide range of composition near stable or metastable eutectics. This fact forces alloys to crystallize into two-phase solids. Because of the need for diffusional sorting of the components and creation of solid-solid surfaces, the kinetics of eutectic crystallization are relatively slow and may be closely related to the ease of glass formation of these alloys.

Experiments have been reported ["Eutectic Solidification and the Formation of Metallic Glasses," W. J. Boettinger, F. S. Biancaniello, G. M. Kalonji, and J. W. Cahn, Rapid Solidification Processing: Principles and Technologies, Volume 2] on the directional solidification of Pd-6 at. % Cu-17 at. % Si alloys which show the evolution of microstructure as a function of interface velocity. A structure of dendrites and interdendritic eutectic at low velocity ($\lesssim$ 0.25 mm/s) becomes a fine eutectic-like structure at intermediate velocities ($\sim$ 1 mm/s) and finally the alloy forms glass when crystallization is attempted at velocities greater than 2.5 mm/s. Of particular interest is the observation and characterization of sharp interfaces which occur in these latter samples between two-phase crystalline material and the glassy alloy.

Alloy Solidification: Solutal Convection
Subtask 2 of Task 12143

S. R. Coriell, W. J. Boettinger, R. J. Schaefer, F. S. Biancaniello

This research is directed toward an understanding of solutal convection caused by the simultaneous concentration and temperature gradients present during the directional solidification of alloys. Included in this study is investigation of the effects of convection on the microstructure and chemical homogeneity of directionally solidified alloys and of the conditions under which undesirable effects can be eliminated. The chemical uniformity and distribution of phases produced during the solidification of alloys controls essential properties and performance such as fracture and corrosion.

In a recently published article ["Convective and Interfacial Instabilities During Unidirectional Solidification of a Binary Alloy," S. R. Coriell, M. R. Cordes, W. J. Boettinger, and R. F. Sekerka, J. Crystal Growth 49, 13 (1980)], the onset of coupled convective and interfacial instabilities during the directional solidification of a single phase binary alloy at constant velocity vertically upwards was treated by a linear stability analysis. The critical solute concentrations above which convection occurs and the spatial wavelength at the onset of instability were calculated as a function of growth conditions for lead-tin alloys. Very small solute concentrations can give rise to convection, e.g., for an interface velocity of 1 μm/s and a temperature gradient in the liquid of 200 K/cm, tin concentrations greater than 3.2 (10^{-4}) wt. % cause convection. At present, the theoretical effort of this task is directed at developing mathematical models of the fluid flow and resultant solute segregation for conditions for which the linear stability analysis predicts instability. This research is being carried out in collaboration with Dr. R. G. Rehm of the Applied Mathematics Division. Macrosegregation during solidification is commonly treated through use of a stagnant boundary layer thickness δ. However, for directional solidification in a container, there is no theoretical means of calculating δ, and δ is essentially a parameter used to fit experimental data. By solving the relevant partial differential equations numerically, we can predict fluid flow and solute distribution (and hence δ) during directional solidification. Development of numerical algorithms for these calculations is in progress.

Experimental research on the occurrence and suppression of solutal convection in off-eutectic alloys and its effects on the microstructure and macrosegregation has recently been concluded. The results are described in a recently submitted article ["Solutal Convection Induced Macrosegregation and the Dendrite to Composite Transition in Off-Eutectic Alloys," W. J. Boettinger, F. S. Biancaniello, and S. R. Coriell, Met. Trans A]. During upward solidification, liquid composition gradients required to sustain plane front composite growth of off-eutectic alloys provide liquid density gradients which cause convection for alloys with compositions rich in the more dense component. This convection disrupts the normal diffusion controlled growth of the composite and produces undesirable macrosegregation and dendritic structures in solidified samples. The effect of solidification velocity and alloy composition on the extent of macrosegregation was investigated. Experiments were also conducted to determine if these undesirable effects could be eliminated. Static magnetic fields of 0.1 T (1 kilogauss), which have previously been successful in eliminating time dependent convection in liquid metals, do not affect solutal convection and do not reduce macrosegregation. Solidification downward (liquid below solid) virtually eliminates macrosegregation but is technically difficult and may be ineffective for large diameter samples (> 3 mm) because of the long-range density gradient induced by temperature.

Additionally, experimental study of convection during unidirectional solidification is directed toward a confirmation of the predicted conditions for the onset of convective flow. Because there are presently no methods for measuring small-scale convective flows in opaque materials, the experiments are carried out with a transparent material in which fluid flow can be observed directly. After evaluating several measurement methods, including laser doppler velocimetry, it was concluded that the most information could be obtained by the photographic tracking of small neutrally buoyant particles.

Experiments with particle tracking using 25 μm diameter latex spheres (density 1.05 g/cm^3) showed good tracking of convective flow patterns but gradual settling out of the particles. Therefore particles with smaller diameters (2.0 μm) and lower density (1.02 g/cm^3) have been obtained. The density of the convecting fluid is 0.98 to 0.99 g/cm^3.

The material used in these experiments is succinonitrile, an organic substance which has been used extensively for analog studies of metallic solidification. Most of the important physical properties of this material have therefore been measured with considerable precision. The experiments require the addition of a solute which is lower in density than the succinonitrile, and ethanol has been chosen on the basis of its similar molecular structure. The experiments require as a first step the measurement of some of the properties of this binary system, and these measurements are in progress. Measurements at low concentrations of ethanol must be made under vacuum because air constitutes a significant contaminant, but preparation of samples of known concentration under vacuum is difficult because of the widely different vapor pressures of succinonitrile and ethanol. Procedures for preparing such samples have now been developed.

Ultrasonic Measurement of Solid/Liquid Interface Position
Subtask 3 of Task 12143

R. L. Parker

Recent tests performed in the NBS Metallurgy Division, using a pulse-echo ultrasonic flaw detector to measure the position of the interface in a melting or freezing tin specimen, indicate that this method offers the possibility of precise, *in situ*, real-time, nondestructive and remote-reading measurement of solidification or crystal growth in opaque substances such as metals or semiconductors.

In order to estimate the amount of reflected sound to be expected from the solid/liquid interface of a metal, one must determine the acoustic impedance $Z = \rho c$ for each phase (solid and liquid) where ρ is the density and c is the velocity of sound for longitudinal (compressional) waves. For a number of metals the velocity of sound is about 10 percent less in the liquid than for the solid, and the density is 3 to 5 percent less. Thus the acoustic impedance is 13 to 15 percent less for liquid than for the solid, and from a simple formula for reflection at normal incidence one can calculate that about 10 percent of the pressure of the incident wave is reflected in the case of solid/liquid tin.

The tests were made on 99.9 Sn at 5 MHz. The transducer contacts the cold end of a 8 mm diam. x 200 mm long specimen in a graphite mold in a Bridgman gradient furnace (unidirectional melting/solidification). Sharp echos easily locate the interface position, to ± 1 mm, over the range of velocities tested to $\sim$ 4 mm/min). Some tests were also made at 2.25 MHz from the liquid side, in larger specimens, with similar results.

Further NBS work will attempt to identify measurement factors inherent in use of the method for measurement, feedback, or control in either industrial or laboratory solidification applications such as continuous casting of metals or the solidification of solar photovoltaic materials. Such factors may include signal generation and detection, frequency effects and attenuation, interface modeling effects, and spectrum analysis and correlation techniques. Appropriate signal processing techniques should make it possible to improve signal/noise ratios and to isolate the characteristics of the solid/liquid interface from such factors as the transducer response or attenuation in the adjacent material.

Surface Tensions and Their Variations with Temperature and Impurities
Subtask 4 of Task 12143

S. C. Hardy

The surface tension of liquid gallium has been measured from the melting point to over 600 °C using a contained sessile drop technique. The measurements have been performed in high vacuum and in atmospheres of hydrogen with the drops resting in cups of a variety of different materials, i.e., pyrex glass, quartz, alumina, boron nitride, and graphite. The cup material has proved to be critical in these measurements because reaction with the liquid gallium or diffusion of impurities from the cup leads to contamination of the sessile drop. This is seen as a surface tension depression at low temperatures due to surface adsorption of these impurities. Consistent and reproducible surface tension values were obtained only with cups of ultra high purity graphite which had been baked at 900 °C for several days in high vacuum before forming the sessile drop under flowing nitrogen. The same surface tension variation with temperature was measured in high vacuum and static reducing atmospheres of hydrogen for these cups. A non-linear least squares analysis of the data showed that the surface tension could be described as follows:

$$\gamma = 709.9 + 0.0016\ (T-29.87) - 0.0000923\ (T-29.87)^2$$

where the surface tension γ is expressed in units of mJ/m^2 and the temperature T in °C. The surface tension of gallium measured with quartz cups in hydrogen closely followed the above function also. With quartz cups in vacuum, however, the measurements indicated surface adsorption at low temperatures. The impurity is probably an oxide which is effectively reduced in hydrogen but not by heating in vacuum. The results described by the above relationship are in excellent agreement with two previous measurements when inaccuracies in the density data used in those works are taken into account.

In addition to the surface tension measurements, we have made extensive observations of liquid gallium surfaces in an Auger spectrometer in collaboration with Dr. Joseph Fine of the Surface Sciences Division. Oxygen and carbon have been found to be the major impurities on the gallium surfaces. After heating, these impurities are segregated into thin patches which float on the surface. Argon sputtering of the liquid results in a complex fluid flow which brings the impurity islands into the ion beam where they are sputtered away. In this way it has been possible to produce gallium surfaces which are free of impurities and remain so within our measurement capabilities for many hours. Although the configuration of the Auger spectrometer is not ideal for sessile drop measurements, several such measurements made at the melting point for sputtered clean surfaces gave values near the result cited previously, i.e., about 702 mJ/m^2. An Auger spectrometer designed for simultaneous surface tension measurements is nearing completion and will be used to study segregation of various species at the surfaces of pure liquid metals and alloys of low vapor pressure.

Diffusion Kinetics
Subtask 5 of Task 12143

J. R. Manning, D. B. Butrymowicz, J. W. Cahn

Because of crystal defects, diffusion of atoms in alloys often occurs by very non-random processes. A striking example of a non-random diffusion process is the surprisingly fast diffusion of zinc into α-brass at low temperatures found in recent experiments done at NBS. This large unexpected effect can be shown to result from diffusion-induced grain boundary migration, a newly-discovered phenomenon in which the introduction or depletion of impurity atoms by diffusion along grain boundaries makes the boundaries themselves move. Other non-random diffusion effects are provided by flows of vacancies and interstitials through metals. As part of the current work, equations have been developed for the effect that these flows can have on the segregation produced in alloys undergoing irradiation in nuclear reactors. Relations between the actual and effective (random) number of atom jumps as influenced by the defect gradients in these alloys have been developed. Some of the results are similar to those for interdiffusion in alloy coatings. It is found that driving forces arising from these gradients can strongly influence the diffusion equations.

In the diffusion-induced grain boundary migration experiments, copper polycrystalline specimens were exposed at 200 °C to 400 °C to zinc vapor produced from α-brass chips. These temperatures are much too low to allow any significant lattice diffusion. Nevertheless, a rather uniform addition of zinc in the interior of the grains was observed to occur. The explanation proposed for this process is that alloying elements move along grain boundaries and penetrate much more deeply there into the base material than elsewhere. That diffusion then makes the boundaries themselves migrate, leaving alloying elements behind in the region the boundary has traversed. Experimentally this grain boundary migration is found to occur only in the grain boundary diffusion zone and under conditions where a sharp concentration gradient is maintained across the moving grain boundary. Thus, it is expected that the effect will be important at temperatures low enough so that lattice diffusion is negligible but high enough so that grain boundary diffusion still occurs. Grain boundary migration also has been found to accompany rapid de-zincing of α-brass at these low temperatures. Since this process produces an effectively greatly enhanced volume diffusion, it has major implications for surface alloying and coatings, leaching and degradation of surface properties, thin film technology, metal contact integrity, and cellular precipitation. Aspects of this effect that are being investigated include the temperature and composition ranges in which this effect is significant and relations between the diffusion rates, grain boundary migration velocities, and magnitudes of the concentration steps at the grain boundaries.

The effect of defect fluxes in making actual atom jump frequencies differs from those expected under random conditions has been analyzed in terms of the independent atom displacements. These independent displacements are not the individual atom jumps but instead involve a complete series of jumps involving an atom and a particular defect, either vacancy or interstitial. Even though the effective random jump frequencies differ greatly from the actual jump frequencies, it can be demonstrated that the difference between the number of effective jumps in directions with and against the force provided by a defect gradient exactly equals the difference between the actual jumps. Irradiation produces defects in the interiors of alloys and thus produces such gradients. The atom fluxes which give rise to segregation effects are determined, of course, by the differences between the actual atom jumps with and against the defect gradients. The current work provides a prescription for describing this difference in terms of four driving forces which influence the effective jump frequencies in irradiated alloys. Large segregation effects are predicted.

Diffusion in Metals Data Center
Subtask 6 of Task 12143

D. B. Butrymowicz, J. R. Manning, M. E. Read

Many metallurgical processes, such as heat treatment, use of protective coatings, sintering, welding, and gas/metal interactions, depend on an understanding of quantitative data for diffusion. The NBS Diffusion in Metals Data Center provides a unique central source where data from the technical literature involving diffusion and related kinetic reactions are collected, analyzed, and compared. Critical reviews are published and inquiries from the technical community for data on particular alloy systems are serviced. More than 23,000 papers reporting diffusion data now are on file. To allow ready retrieval, these references are classified according to the alloys on which they contain data.

In order to handle this information efficiently, an effort has been undertaken to computerize the bibliographic and classification data in these files. New computer hardware has made it possible to record locally, in machine-readable form, information concerning technical documents. Further steps are being developed to capture bibliographic records from on-line data bases and through local editing capability to add our specific indexing information. A complete file of ternary alloy systems for which diffusion data are available, over 2000 in number, has been input locally onto floppy disks, which are searchable and updatable locally also. The ternary files may now be searched and sorted in various ways not possible previously when purely manual techniques were used.

A compilation and critical evaluation of thirty-three candidate hydrogen-storage materials for eighteen different physical and chemical properties, including reaction rates, diffusion coefficients, and other kinetic properties has been completed. This project carried out jointly with personnel from the NBS Alloy Data Center resulted in 660 data sheets being prepared. This information will be disseminated by Lawrence Livermore Laboratory, where an on-line data base for these materials is being established.

Further funding was received from the International Copper Research Association (INCRA) for compilation and critical evaluation of diffusion data in selected copper alloy systems. This project is part of a continuing program with the copper industry's trade association to provide it with handbook data pertinent to transport processes and relevent to research and development activities of this industry.

Cooperative efforts with Argonne National Laboratory were initiated to bring about the collection and evaluation of transport data in stainless steels employed in reactor systems. The Data Center has already within its files a large fraction of the world's literature pertaining to these critical alloys and efforts are being made to integrate our evaluation activities with the experimental activities, leading to a recommended set of diffusion rate values for substitutional stainless systems.

<u>Metals Processing Laboratory</u>
Subtask 7 of Task 12143

W. J. Boettinger, F. S. Biancaniello, J. C. Orbock, S. D. Ridder, R. J. Schaefer, R. D. Shull

The primary research endeavor of this laboratory is new and innovative metals processing technology. Some of these processes include electron beam surface melting which produces rapidly solidified surface layers. These layers are used both for the study of the effects of rapid solidification on microstructure and for wear and abrasion studies. Also, a vacuum melt spinning device is being constructed to produce rapidly solidified ribbons for the study of the morphology and structure of bulk metallic glasses and metastable crystalline compounds. Another new area includes the design and construction of a device for the measurement of convection and segregation during semi-continuous castings of low temperature alloys under axi-symmetric heat flow conditions.

A program conducted in the Metals Processing Laboratory during the past year is concerned with the metallurgical processing of aluminum alloys. This task simulated industrial casting and thermomechanical processing practices in the production of 2219 aluminum alloy. Such alloys have been the subject of concern in the aerospace industry. The objective of this research was to elucidate the relationships between macrosegregation, microstructure, and mechanical properties.

This investigation involved special casting geometry to simulate industrial macrosegregation characteristics and subsequent examination of these cast ingots to determine the effect of chemistry variations on properties. Thermomechanical processing of as-received 2219 plates was performed to obtain data necessary for determination of Time-Temperature-Transformation diagrams and C-curves. Also an ingot of directionally solidified Θ phase (Al_2Cu) was prepared for microprobe studies.

A major effort has been the modernization of the entire laboratory. A data acquisition system has been ordered to simplify data collection, manipulation, and experimental control. The entire heat-treating part of the laboratory is being consolidated and temperature control modernized.

A summary of the past year's activities supporting other programs follows:

- Prepared $Pd_{77}Cu_6Si_{17}$ and related alloys for rapid solidification studies and for phase identification of the resulting microstructures. Silver-copper eutectic was prepared in conjunction with this research.

- Prepared a series of dilute Al-Ag alloys for determining planar vs cellular growth at high velocities obtained by rapidly scanning in electron beam.

- Prepared Cu 15 w/O Ag, Cu 3.5 w/o Al and Cu 7 w/o Al alloys for sliding wear test materials for studies on microstructures relating to the friction and sliding wear behavior of metals.

- Prepared 1020 steel for abrasive wear tests.

- Prepared O-2 tool steel and pure copper for pin on disk wear tests.

- Prepared Ti-Al alloys (with and without Mo and Nb) in conjunction with an effort to determine the Ti-Al phase diagram and the effects of adding β-stabilizing elements.

- Prepared Cu-Ga-Ge alloys as part of an investigation to determine whether massive transformations require nucleation at grain boundaries.

- Prepared directionally solidified $AuIn_2$ and zone refined $AuAl_2$ boules for use in superconductive devices for temperature fixed points.

- Prepared Ni-Al alloys and Ni 8 w/o Al single crystal for neutron diffraction studies.

- Prepared ultra thin foils and various heat treatments on metals and alloys in support of other Division activities.

ALLOY DURABILITY FOR WEAR APPLICATIONS
Task 12144

The activities in this task are directed toward the measurement of the properties and performance of alloys that are used (1) in service under wearing conditions and (2) in applications as synthetic implants in humans. Primary emphasis in both areas is directed toward improved methods of properties measurement and testing of alloy performance under appropriate conditions. Further, considerable emphasis is directed toward the need for better fundamental knowledge and accurate, useful data on the mechanisms and processes of wear, fatigue, corrosion, and fracture of metals as they apply to these uses.

The impact of the wear processes on U.S. technology in terms of lost productivity, loss of critical materials, safety and general economic costs has been estimated to be in excess of $30B to $50B per year. While wear is an extremely complex phenomenon, frequently involving several interacting mechanical and chemical processes, it is generally agreed that an improved understanding of the materials science aspect of the problem should offer the best opportunity to control wear costs. Efforts in this task are selected with this consideration in mind. An increased effort in this task has resulted from the FY80 Durability initiative, permitting the addition of three technical staff members. New projects have been initiated in the areas of galling wear, fatigue wear, and abrasive wear of composite materals. Task personnel hold leadership positions in the ASTM Committee G-2 on Erosion and Wear in order to ensure the effectiveness of our contributions in measurements and standards to industry. One of our staff holds a patent on a newly-developed wear resistant alloy. Another staff member is Program Chairman for the Third International Wear of Materials Conference scheduled for early 1981 at which over 125 research papers on various aspects of wear are scheduled for presentation.

In the area of synthetic implant materials science, task members organized and carried forward at NBS an International Conference on Implant Retrieval this spring. At this meeting, leading research scientists and physicians described the current state of understanding of implant failure and success in service. The emphasis in our research program on fatigue, corrosion, and compatability characteristics of implant alloys is completely consistant with the emphasis presented at this Conference and the Workshop that followed it. In this area also, task members provide significant leadership on the ASTM-F4 Committee on Medical and Dental Materials and Devices to insure effective contribution to the needs of the industry and the public.

The task is divided into four subtasks whose activities and accomplishments over the past year will be described next. These subtasks are: Mechanisms of Metallic Wear, Lubricated Wear, Wear Standardization and NDE, and Metallic Biological Implants.

Mechanisms of Metallic Wear
Subtask 1 of Task 12144

A. W. Ruff, L. K. Ives, P. Blau, K. J. Bhansali, F. Matanzo

Several projects in this subtask are studying the mechanisms of wear under different conditions of dry sliding and abrasion. It is necessary to carefully design these experiments in order to avoid complications due to multiple wear modes acting and possible environmental complications. One project is examining the effect of mechanical properties changes in several steels and copper alloys on the plastic deformation mode of wear. A computer controlled block/ring wear test machine is used. The alloy specimen is maintained in an argon atmosphere during wear to control environmetal interactions. Wear tests are carried out at fixed load and speed for total sliding distances up to 700 meters. Both friction force and wear displacement are continually recorded and stored as digital data. This permits subsequent data smoothing and correlation analysis. Wear debris is recovered from these experiments for examination along with studies of the worn surface and subsurface microstructure. Results have been obtained so far on three different steels (a tool steel, low carbon steel, and dual-phase steel) and on copper and two copper-aluminum alloys. Mechanical properties measurements of the work hardening characteristics of the steels have also been made for comparison with the wear data. Results indicate that when plastic deformation processes are the dominant mode of wear, the tendency for an alloy to accommodate larger amounts of plastic strain at a given stress level is reflected in a lower wear rate. A wear debris formation mechanism has been identified that involves the repeated deformation and eventual ductile failure of surface protrusions. The dual phase steel alloy appears capable of accommodating greater amounts of wear deformation before metal is detached to form wear debris. A talk describing these results was presented at Cornell University this spring. Future plans include studies of several other steels exhibiting extended ductility under multiaxial loading conditions. Electron microscope methods will be applied to measure the depth of wear damage and the effect of microstructure such as grain size and orientation on the distribution of subsurface damage.

Abrasive wear mechanism studies are being carried out on steel and on surface modified alloy specimens. Low carbon steel specimens have been heat treated to produce different microstructures so that the influence of phase type and distribution can be examined. The effect of small amounts of water (400 ppm and less) on the abrasive wear of steel is being studied. A cooperative study with the Naval Research Laboratory of the abrasive wear process in surface modified alloys is underway. Laser surface melting of aluminum, nickel-based, and titanium alloys is carried out and particles of tungsten carbide and titanium carbide are injected into the melted surface before it is rapidly solidified. This process forms a composite surface layer having a hard phase particle concentration up to 50 percent by volume. The abrasive wear resistance is increased up to 50 times. Studies of the effect of particle size, spacing, type, and alloy composition and structure will be carried out to better understand the abrasive wear mechanism in these composite surface layers.

Another phase of this work deals with the role of microstructure in determining the wear-in behavior of metal surfaces. A computer controlled, stroke-by-stroke wear and friction tester was built to study the manner in which microscopic changes at and beneath sliding surfaces affect the rate and severity of surface deterioration. Computer graphics methods are used in the analysis of a time record of friction changes at selected locations on the sample surfaces. Effects of test environment, microstructure and material composition were seen to strongly influence wear-in behavior of copper, aluminum, bronze, and several steels. Continuing studies for the coming year will address crack initiation and propagation in worn surfaces during the wear-in period.

A new project is cocerned with the mechanisms of scuffing and galling wear. These wear processes frequently render parts of components of mechanical systems inoperative even though very small amounts of material have been removed. Under lubricated conditions, failure of the lubricant and associated scuffing causes localized wear which often causes total breakdown of the lubricant. Very little is known about the influence of basic materials properties on scuffing and galling wear. In the past, selection of materials for a wear couple has proceeded mainly on an experimental basis. Such a selection process invariably leads to overdesigned systems as well as specification of expensive alloys which use critical strategic metals, e.g., cobalt base alloys. This project will examine the detailed mechanisms of scuffing and galling. Particular attention will be focused on the influence of intrinsic properties such as stacking fault energy and on the microstructure of the alloys. A simple test unit capable of loading engineering and special alloys up to their yield strengths during sliding is being designed and built. The worn specimens and the wear debris will be characterized by means of scanning and transmission electron microscopy. Attempts will be made to correlate the surface topography, subsurface microstructural changes, and mechanical deformation to intrinsic metallurgical properties of the alloys.

Another new project supported by the U.S. Army Materials and Mechanics Research Center concerns the use of metal matrix composite materials. The interest here is in lightweight composite aluminum alloys for use as structural materials in wearing applications. Aluminum alloys generally offer a low and unacceptable wear resistance. Composites of aluminum alloys with hard particles such as alumina and silicon carbide are expected to offer considerably improved wear resistance in combination with high strength-to-weight ratios. This project is aimed at understanding the wear modes in composites to help select optimum process parameters as well as compositions for maximum benefits.

Lubricated Wear
Subtask 2 of Task 12144

L. K. Ives, A. W. Ruff, M. Peterson, H. C. Burnett

One project in this subtask is directed toward the development and evolution of bench wear tests for the characterization of rerefined engine oils. The project is supported by the NBS Recycled Oil Program which was established in response to the Energy Policy and Conservation Act of 1975. That Act directs the NBS to develop tests to establish the substantial equivalency of recycled oils to virgin base oils. During the past year this project has been concerned primarily with the evaluation and development of tests employing the standard ring and block specimen configuration. Existing ASTM test methods have been examined as have several variants of these methods. Test conditions are carefully controlled and the friction and thermal response of each oil under investigation is monitored and recorded. An important component of the evaluation procedure involves the examination of worn metal surfaces by means of scanning electron microscopy. These studies are aimed at relating metallurgical and surface morphological characteristics to the wear test response of different oils. Some initial results of this work were presented in an invited paper at the 1979 conference sponsored by the Recycled Oil Program, ASTM Technical Division P, and the Mechanical Failures Prevention Group. Current studies indicate that one test method, the Suntech Timken Method, is especially promising with respect to the characterization of the wear response of engine oils. Through application to a series of IIID engine sequence test reference oils, it has been found that the Suntech Timken test is capable of discriminating among these oils and ranking them in agreement with their known performance. Moreover, these results are of particular significance because they can serve as the basis for the construction of a reference scale to which the behavior of oils having unknown performance may be compared. Based on this approach studies are currently underway to determine the extent to which additive response of selected recycled base oils may be determined for different metallurgical combinations. In a related activitiy, personnel from the Postal Service Research Laboratory have visited our laboratory to examine the test methods developed here for lubricated wear studies in connection with a serious wear and failure problem experienced in their operations.

A second project, supported by the Office of Naval Research, concerns the study of the friction and wear properties of an experimental solid lubricant, $SbSbS_4$. This compound has an amorphous structure and is obtained in the form of a finely divided powder. When applied as a grease additive $SbSbS_4$ has been reported to confer outstanding anti-wear and anti-seizure capacity--much in excess of that achieved with MoS_2 and most organic additives--in four-ball and pin and V-block tests. These results have been confirmed in our own studies. Our work seeks to understand the mechanism by which $SbSbS_4$ functions as a lubricant, the extent to which the compound may serve as a lubricant for various metals in contact including stainless steels, and the range of contact conditions of load, speed, and temperature over which it is effective. Preliminary differential scanning calorimetry examination and thermal decomposition studies suggests that the availability of active sulfur to react with the metal surface plays an important role in the function of $SbSbS_4$. In typical wear tests conducted with the pin and V-block and four-ball test machines, contact temperatures are characteristically high and $SbSbS_4$ as a grease additive is very effective in reducing friction and wear. When a ring compression friction test was used, however, $SbSbS_4$ was found to be relatively ineffective as a lubricant--far less so than MoS_2, for example. In the ring compression test relatively high stresses are achieved at the metal-metal contact without an accompanying rise in temperature. To extend these studies of the friction and wear characteristics of $SbSbS_4$ to cover a wider range of contact conditions, a pin-on-disk test machine capable of elevated temperature operation, low sliding speeds and high loads has been designed and constructed. Additional studies utilizing electron microscopy are underway to investigate the structure of $SbSbS_4$ before and after exposure to sliding contact. Electron microscopy studies of the composition and structure of worn metal surfaces are also planned. The mechanism of wear and friction reduction by this compound on different alloy surfaces should be determined through these various approaches.

Task members provide leadership to the Mechanical Failures Prevention Group which stimulates voluntary cooperation among all segments of the national scientific and engineering communities in efforts to reduce the incidence of mechanical failures and to develop methods to predict mechanical failures. During FY80 the MFPG was involved in two conferences; a joint conference on Measurements and Standards for Recycled Oil/Systems Performance and Durability, and a conference on Failure Prevention in Ground Transportation Systems. Both Conferences were held at NBS and were well attended. They provided good opportunity for technical discussions in these important areas. During FY81 two technical conferences are planned. These involve the subjects of: "Detection, Diagnosis, and Prognosis: Contributions to the Energy Challenge," 7-9 October 1980, Los Angeles, California, and "Aircraft Maintenance Technology," 21-23 April 1981, NBS, Gaithersburg.

Wear Standardization and NDE
Subtask 3 of Task 12144

A. W. Ruff, L. K. Ives, P. J. Blau

One project is concerned with the development of metal standard reference wear test specimens for an abrasive wear test that is widely used in industry. Abrasive wear is one of the most frequently encountered forms of wear. In industry it has been estimated that perhaps 50 percent of all wear can be traced to this source. Excavating, mining, and agricultural machinery as well as a variety of equipment used in processing and handling abrasive material must be designed to minimize abrasive wear while maintaining the structural integrity associated with other functions. Accurate data and appropriate test procedures are necessary both for equipment design purposes and to assist in the development of more economical and/or improved materials. The dry sand/rubber wheel abrasive wear test is found to yield results that correlate well with service behavior when the stresses imposed on abrasive particles are relatively small, i.e., appreciable fracture and crushing of the abrasive do not occur--and when the abrasive particles are not rigidly supported. Following nearly five years of effort, the ASTM Committee G-2 on Erosion and Wear has developed an approved standard method for the dry sand/rubber wheel abrasive wear test. Project staff members have made significant contributions to that effort both in writing the standard and through participation in several round-robin test series.

Development of suitable reference specimens for this test method is now underway at NBS. This effort involves the selection and preparation of appropriate materials and the demonstration of good repeatability in the test results. As a prerequisite to realizing these goals it has been necessary to carry out a detailed evaluation of the test procedure and to determine the influence of several test variables on measured wear rates. On the basis of our own studies and the recommendations of other G-2 Committee members employing the dry sand/rubber wheel test, two materials, D-2 tool steel and 1020 carbon steel, have been selected for development as SRM's. Tentative arrangements have been made for the manufacture of one thousand D-2 tool steel specimens which will be sold as abrasive wear reference specimens by NBS. It is anticipated that similar arrangements can be made for the preparation of 1020 steel reference specimens in the near future. Plans for next year also include a new effort to evaluate abrasive particle characteristics (as well as metal wear debris particles) using quantitative metallographic methods. Future development of reference abrasives for uniformity in wear testing methods will be explored.

Another project is concerned with the nondestructive monitoring of wearing systems and is supported through the NDE office. Two approaches are used in this work: (1) a study of wear debris particles in order to identify the type and severity of wear taking place in an operating system, and (2) the application of acoustic emission detection techniques to monitor fatigue or delamination wear modes in metals. An instrumentation system has been assembled this year to apply acoustic emission methods to a block/ring wear tester. The system involves a broad-band AE transducer, a variable gain amplifier and filter system (up to 100 db gain), and a modified video tape recorder. Specimens containing preexisting cracks in the wear-affected zone will be studied. Noise and emission spectra will be recorded and then played back through the Division's AE signal processing equipment to identify and quantify relevant signals. Spectral analysis and fourier transform methods will be applied.

Metallic Biological Implants
Subtask 4 of Task 12144

A. C. Fraker, A. W. Ruff, G. J. Mattamal, J. S. Harris, A. C. Van Orden, G. A. Danko

Recent times have seen considerably increased use of metals as surgical implants. Research efforts and clinical studies have been applied to produce improved performance implant materials. This is evidenced in the increased use of titanium alloys and improved cobalt-chromium-molybdenum alloys (hot isostatically pressed; forged). The purpose of this subtask is to study metals currently used or considered for use as surgical implants. Mechanical properties and chemical reactivity are investigated to obtain data on corrosion behavior, corrosion-fatigue life, wear, fretting, and metal-protein interactions. Variations in heat treatment and in some cases, the application of surface coatings are used in an effort to improve implant materials. Drs. Pei Sung and M. Ashraf Imam participate in this project as guest workers from the FDA and George Washington University, respectively. The collaboration with Dr. Imam deals with mechanical property and corrosion fatigue studies and how these are affected by changes in the microstructure. One investigation with Dr. Sung was completed recently and this dealt with coupling of dissimilar metals to utilize the best properties of each for the implant. From the standpoint of corrosion behavior, it was determined that the designated implant alloys of cobalt-chromium-molybdenum, cobalt-nickel, and titanium-6 aluminum-4 vanadium probably would be acceptable as coupled materials. Continuing research with Dr. Sung will deal with repassivation of individual metals and with effects of surface ion implantation of carbon, nitrogen and boron. Techniques employed in this work include potentiostatic polarization, transmission and scanning electron microscopy, ultra filtration of proteins, atomic absorption, calorimetry measurements, and torsion fatigue testing.

Studies on the relatively new titanium Ti-4Al-1.5Mo-1.5 Cr alloy which is being considered for implant use, have been carried out in three areas: microprobe analysis, microstructural study using transmission electron microscopy, and corrosion behavior study. The purpose is to determine the extent of alloy inhomogeniety and to identify the phase structures and distribution. Microprobe analysis was performed on samples after three different heat treatments. The exact chemical composition of the phases was determined. The analysis showed the matrix composition of the two phase samples to be lower in Ti and Al and higher in Mo and Cr. Samples of four different heat treatments of the material were examined using transmission electron microscopy which allows detailed microstructural study of the material including electron diffraction. Anodic polarization measurements have been conducted to study the behavior of the alloys in simulated body saline solutions. Specimens of several different heat treatments of the material have been studied. More anodic polarization tests are planned including tests to determine the effect of Mo and Cr in the alloy on the corrosion behavior in a solution containing the amino acid, cysteine, which has a sulfur containing ion. A pitting corrosion test for an ASTM round-robin test was also carried out on a 316 stainless steel alloy. Future plans include the study of several cobalt-based alloys using these techniques. We will also explore the possibility for a reference material to be provided by NBS for use in a standard method for crevice or pitting corrosion being developed by ASTM.

A major accomplishment this year involved setting up a torsional corrosion-fatigue machine for studying the fatigue life of implant metals. Tests are being conducted under fully reversed torsion at a constant shear strain amplitude and frequency of 1 Hz in a flowing physiological saline solution at 37 °C and pH of 7.4. The effects on fatigue strength of changing the alloy microstructure through heat treating and quenching are being determined. The Ti-4.5Al-1.5Mo-1.5Cr alloy and the improved cobalt-chromium alloy in the forged high strength and micrograin conditions are being studied at George Washington University and at NBS. This is a cooperative program involving Dr. M. A. Imam of the George Washington University. A scanning electron microscopy study of the fatigued specimens has been initiated to give an insight to the complex relationship between environment, loading mode, and microstructure. Emphasis is being placed on the failure mechanisms and identification of crack initiation sites. A transmission electron microscopy study is being conducted to determine if transformations in the microstructure occur under the cyclic loading condition. Results from the fatigue tests were published in the Proceedings of the 4th International Conference of Titanium in May, 1980, in Kyoto, Japan.

An investigation is underway to study the binding of metal ions to proteins in human blood albumin (HBA) in connnection with the general problem of implant alloy compatiblity with the human system. Measurements are being made of the concentrations of bound nickel ions in HBA. Methods of ultrafiltration and atomic absorption spectroscopy are being used. Microcalorimetry techniques are also being applied to the determination of the bond energy involved. Preliminary results have been obtained for the heats of reaction involving both a 3 percent HBA protein solution and a 3 percent amino acid solution with solutions containing from 10 to 100 ppm Ni. Potentiometric titration studies are planned for next year to supplement the data from these other methods.

A second study of metal-organic reactions has been undertaken in which we are concerned with potentiostatic corrosion of 316 L stainless steel in a human serum albumin (protein) solution. The amount of chromium and other ions released into solution from the alloy are quantified through the use of atomic absorption spectrophotometry to determine the efficiency of the reactivity of implant materials in vivo and their relationships to human metal ion sensitivity and failure modes such as corrosion fatigue.

Fretting wear studies of implant alloys are being planned for the near future. Two different apparatus have been designed, constructed, and tested for exposing implant alloy specimens to simultaneous fretting wear and potentiostatically controlled corrosion. Both apparatus simulate the geometry and conditions present at a screw-screw hole interface such as is found in many fracture fixation devices. In one system a rotating fretting motion is applied; in the other system, a rocking fretting motion is applied. It is possible to control the loads and amplitudes of the fretting wear motion as well as the solution chemistry and electro-potential. The wear debris produced during the experiments can be recovered and studied along with the worn surfaces. Since fretting processes are characteristically slow under actual conditions, experiments will be carried out for long terms of several hundred hours. Current efforts involve the design and construction of a digitally controlled, computer interfaced potentiostatic system for the fretting experiments. The system would permit continuous monitoring of the experiments and alteration of test conditions as appropriate.

CHEMICAL METALLURGY FOR DURABILITY
Task 12145

The interplay between thermodynamic predictive models and the formation and stability of alloy phases is the central theme of this task's activities. This theme is developed in data, theory, and experiment. Conventional and new experimental techniques are combined with theoretical models in the determination and prediction of phase diagrams. Special emphasis is placed on the development of on-line computer graphic systems. In addition to its fundamental scientific interest, advancement in the understanding of phase diagrams is essential to permit greater flexibility in development of new alloys for improved performance, ease of processing, reduced cost, and energy use, as well as in providing substitutes for scarce elemental additions.

A joint effort mandated by agreement between the Directors of the National Bureau of Standards and the American Society of Metals (ASM) has been undertaken to provide critically evaluated phase diagram and other constitution data as well as related bibliographic material. Technical oversight of this program and work on selected systems is being carried out by the Alloy Data Center (supported in part under this task and by the Office of Standard Reference Data). ASM continues to support a Research Associate at NBS for this project. A semi-annual Bulletin of Alloy Phase Diagrams is also published under this program.

The phase diagram of the Ti-Al system is being studied experimentally with a number of different techniques as a part of a Navy program to improve titanium processing technology. In addition, phase diagram data are being exploited in the solution of problems in areas of critical national need; for instance, materials are selected for study as electrocatalysts in hot phosphoric acid on the basis of available phase constitution data; here, surface phase stability is of utmost importance. In fair measure, the task members' established scientific competences are challenged and stimulated in the course of this work; for example, studies of alloying led to fundamental inquiry into the definition of electronegativity concepts; catalysis research on non-noble alloys required better understanding of the electronic structure of refractory hard metals and of the definition of charge transfer in these materials; modeling of thermodynamic functions, necessary for phase diagram prediction and an aid in critical evaluation, led to development of a method for applying d-electron energy band parameters to prediction of heats of formation of transition metal alloys. Mössbauer techniques have been used to quantitatively identify phases in several materials. New results have been obtained in a DOE-DOD fuel cell catalyst program. We are working on the NASA soft Al project focusing on the understanding of both stable and metastable phases produced by processing, and devising methods for nondestructively detecting them by hardness, eddy current, and positron annihilation measurements. New work on the latter completed this year is described under "Alloy Properties Science for Structure Characterization." The new initiative on materials processing includes proposed phase diagram work. Task workers are strongly involved in committee work including Chairmanship of the Committee on Alloy Phases of the Metallurgical Society of AIME.

Our work is described in more detail in the following three sections: Alloy Phase Stability, Alloys for Fuel Cells and Catalysis, and Nondestructive Evaluation of Nonuniformities in 2219 Aluminum Alloy Plate Relationship to Processing.

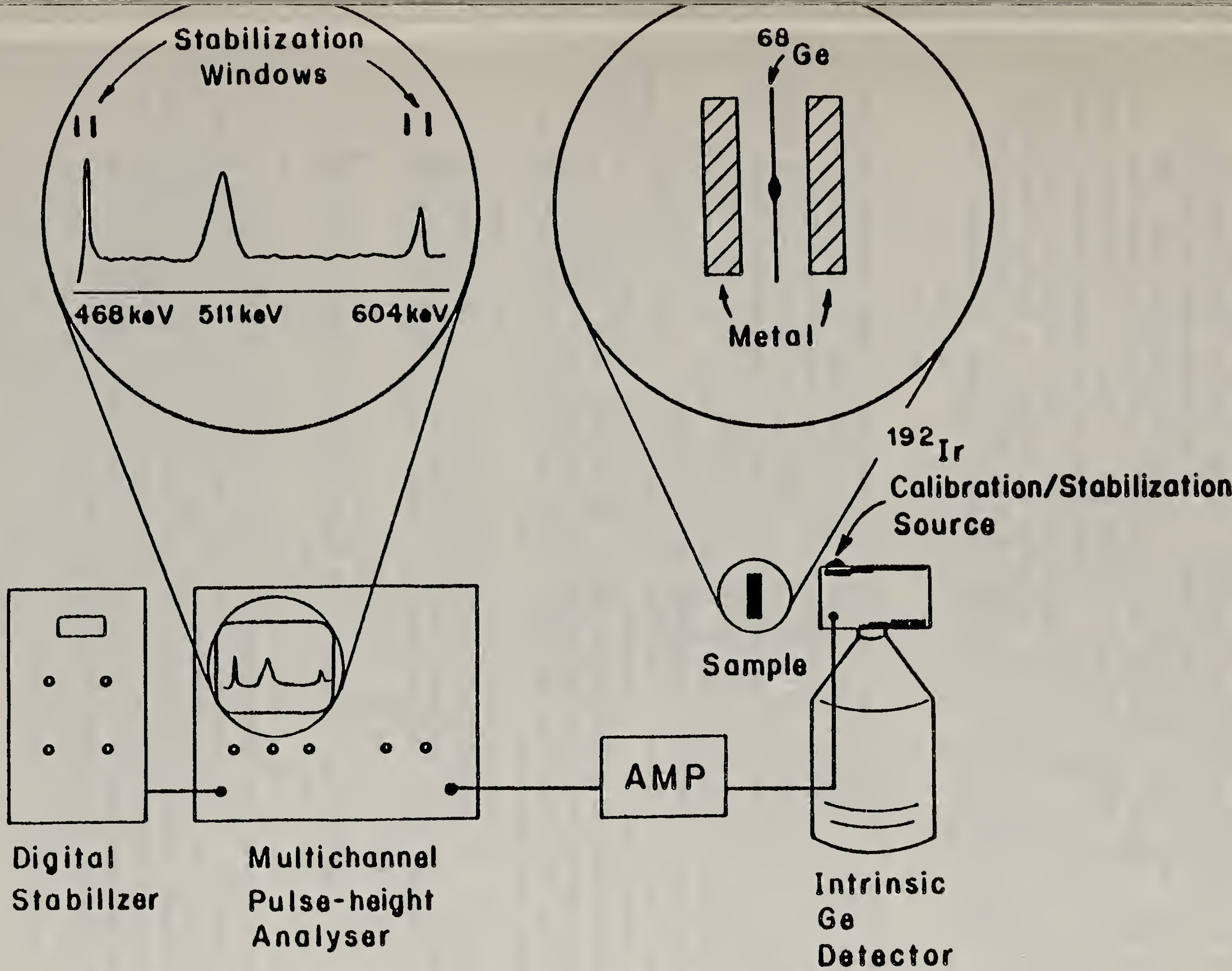
<u>Alloy Phase Stability</u>
Subtask 1 of Task 12145

L. H. Bennett, J. R. Cuthill, J. L. Murray, L. J. Swartzendruber, R. Shull

We are pursuing a program of three interconnected parts: critical data evaluation and compilation of phase diagrams; experimental phase diagram work on systems selected to support the evaluation program; and the theory of alloy phase stability, this year stressing application of energy band theory to the prediction of the heat of formation of alloys.

The Alloy Data Center has established a collaborative alloy phase diagram critical evaluation program with the ASM. This joint effort has two key aspects: (1) development of an on-line indexed bibliographic system starting with the current ASM automated system for the METADEX data base; and (2) the organization and preparation of critical compendia for binary and multicomponent alloy phase diagrams. On the first aspect, significant improvements have been made in the METADEX system, including more thorough scanning of literature sources and more extensive indexing, and a contract has been let to provide separate, quicker access to the subset of alloy phase diagram data. To achieve the second aspect of this joint program, an International Council of distinguished experts has been established to advise on various aspects of the critical evaluation effort, and panels formed to deal separately with binary and higher order systems. In the binary effort, Joanne Murray has been appointed Category Editor for Ti. A first set of ten evaluated systems should be ready for publication by October. These systems include Ti-Sc, V, Cr, Y, Zr, Nb, Mo, Hf, Ta, and W. A bulletin, Alloy Phase Diagrams, will be published; the first number is in proof, and the second in preparation. During the current year, considerable progress has been made in the development of software for on-line graphic display of phase diagram data through application of spline fitting techniques to published phase diagram data. The program now available plots camera ready, publication quality phase diagrams, and has a user oriented input procedure. An invited talk describing our progress in phase diagram graphics was presented at the 1980 CALPHAD meeting. Several groups expressed strong interest in obtaining our program or in visiting NBS to make use of our graphics facilities. A database management program for the graphics files is now under development. A Research Associate supported by ASM has spent another summer with us, editing materials amassed under the auspices of OSRD and other agencies for a comprehensive, complete revision of the Hansen phase diagram compilation.

Of course, we are not attempting to evaluate all systems ourselves at NBS. Evaluations will be carried out throughout the world at institutions recommended by the International Council. Priorities will determine which important classes of systems are evaluated first. At NBS, we are



Positron Annihilation
(Doppler Broadening)
Gamma-ray Spectrometer

Figure 1. Experimental Apparatus for Doppler-Broadened Lineshape Measurements. The positron source is 25 microcuries of ^{68}Ge. An ^{192}Ir source is used to calibrate the energy scale and maintain system stability.

Other experiments of fundamental significance to phase stability are underway. Dr. David Goodman, a Postdoctoral Research Associate, is investigating the thermodynamic properties of Ti-Al alloys using a solid electrolyte electrochemical technique. Dr. R. C. Reno is spending a sabbatical year with us, and will be working on the application of the positron annihilation technique to phase boundary determination in Ti and Ti-Al alloys. An earlier collaborative study with Dr. Reno of defects in Ti by the positron annihilation method was published this year. Preliminary differential scanning calorimeter studies on Ti-Al, directed at determination of the $\alpha/\alpha - \alpha_2$ phase boundary, have been carried out. Metallic glasses and metastable crystalline compounds are another class of material of great interest. They have often been found to possess certain more desirable properties (e.g., corrosion resistance, strength, hardness, and ductility) than their equilibrium counterparts. In pursuit of this interest, a vacuum melt spinner is being constructed, wherein the molten alloy is solidified very quickly by impinging the liquid onto a copper wheel rotating at speeds around 10,000 rpm. By this process, quenching rates on the order of 10^5 degrees/s are typical.

The major thrust of our theoretical studies in the current year has been the use of electron band theoretical parameters in the prediction of the heat of formation of binary alloys. The predictive scheme, devised in collaboration with Dr. R. E. Watson, was described in a paper published in Physical Review Letters this year. Two invited papers describing this work were presented at the 1980 CALPHAD meeting. In one, a database of enthalpies of formation for 60 of the 276 possible binary pairs of transition elements was presented. In a second paper, the experimental data were used for a constrained least squares adjustment of the theoretical band parameters. Discrepancies between the resulting predictions and the experimental data, where such data exists, are less than the uncertainties in the data. The Proceedings of the Theory of Alloy Formation organized and held at the New Orleans AIME meeting was published this year.

Prof. T. B. Massalski is visiting us this year. He serves as Chairman of the International Council's Panel on Binary Alloys, and participates actively in our program. He has recently been elected to the Polish National Academy of Sciences.

J. R. Cuthill has recently been made a Fellow both of the ASM and the ASTM.

Our activity in ASTM continues. Task workers participate in ASTM Committees D32 on Catalysis, E42 on Surface Analysis, E13 on Molecular Spectroscopy, B5 on Cu and Cu Alloys, and E7 on Nondestructive Evaluation. L. H. Bennett serves as Chairman of the Committee on Alloy Phases of the Metallurgical Society of AIME. L. H. Bennett and J. R. Cuthill are the official NBS representatives on the Joint ASTM-SAE Committee on the Unified Numbering System in Metals and Alloys.

Alloys for Catalysis and Fuel Cells
Subtask 2 of Task 12145

A. J. McAlister

Development of successful fuel cells will significantly increase the efficiency of fuel utilization and markedly reduce our national dependence on foreign energy sources. For low temperature acid fuel cells, a number of problems are performance limiting. Scarce and expensive Pt, now used as both fuel and air catalysts should be replaced or more efficiently used, and air catalyst supports more resistant to corrosion at cathodic potentials are needed. Despite these difficulties, many practical advances are being made. The DOD has successfully employed small cells of a few kilowatt capacity in transportation and portable power source applications, while in the area of power generation, DOE and EPRI have sponsored a 4.8 megawatt, naptha fed assembly which is scheduled for operation on the New York City power net this year.

Many challenging scientific problems are encountered in the area of fuel cell research. In the past, we have focused our expertise in the electronic and physical properties of refractory hard metals, compounds of transition metals with light metalloids, on a search for acid stable, hydrogen oxidation catalysts to substitute for Pt as the fuel electrocatalyst in low temperature acid fuel cells. We observed, for the first time in our laboratory, some measure of activity and voltage stability in Re metal, $W_{0.5}Ti_{0.5}C$, and WP, and strong activity in the ternary $Mo_{1-x}W_xC$ $(1 - x = 0.7, 0.8)$ which is isostructural with the known strong, CO poison-resistant fuel electrocatalyst WC.

Comparative studies of the Mo-rich ternary and WC have been completed. We showed these alloys to be equally corrosion resistant, catalytically active for H_2 oxidation, and CO tolerant. In addition, we demonstrated that proton discharge is rate limiting on these carbides, in contrast to Pt where chemisorptive dissociation is the slow step. This work has been described in a paper accepted for publication in Electrochemica Acta, and in an invited talk at the symposium "Surface Properties of Refractory Metals and Compounds," at the Annual AIME meeting.

Current activity focuses on anode catalysts of Pt dispersed on WC. Pt, like chemically similar Co and Ni, is predicted to surface segregate on WC, perhaps wetting it as well. Surface phases may form, and provide not only more efficient use of Pt, but desirable catalytic properties intermediate to those of highly active but CO sensitive Pt, and less active but CO tolerant WC. We have prepared light loadings (nominal partial monolayers) of Pt on WC. Studies in dilute H_3PO_4 at 23°C show these preparations to be about a tenth as active as similar loadings of Pt on carbon supports in pure H_2, but ten times as active as Pt sheet in H_2 containing 2.9 percent CO. Triangular wave voltammetry and charging curve measurements indicate very high dispersions; surface phase formation is strongly indicated. This work was reported in an invited talk at the 1980 National Fuel Cell Seminar. Electrochemical and thermal stability of these alloys are being investigated via polarization studies in concentrated acid at high temperatures.

In our earlier survey studies of the refractory hard metals, we observed several materials, most notably TaN and TaB, to remain passivated at potentials well beyond the O_2 reduction equilibrium potential. We are testing them for performance as non-corroding Pt cathode catalyst supports.

Two experiments aimed at more thorough understanding of H_2 oxidation on non-noble fuel electrocatalysts via eludication of the geometry of the active sites are underway. In one, studies of H_2 oxidation on the cubic W-Ti-C alloys as a function of metal content are being pursued, to compare the mechanism of the hydrogen reaction with that on hexagonal WC. (Pure TiC is inactive.)

In the other, Raman spectroscopy, which is capable of yielding microscopic information on catalyst surfaces in situ, is being pursued. A Raman cell was completed and tested for chemical and optical performance. Results of direct studies of WC in dilute H_3PO_4 at 23 °C were negative. Impurity modes may be observable on Pt/WC catalysts; several strongly Raman active hydrocarbons are adsorbed on WC and may prove useful in surface titration studies. These possibilities are being pursued.

A. J. McAlister is a member of ASTM Committees E42 on Surface Analysis and D32 on Catalysis.

Nondestructive Evaluation of Nonuniformities in 2219 Aluminum Alloy Plate--Relationship to Processing
Subtask 3 of Task 12145

L. J. Swartzendruber, L. K. Ives, W. J. Boettinger, S. R. Coriell, D. B. Ballard, D. E. Laughlin, R. B. Clough, F. S. Biancaniello, P. J. Blau, J. W. Cahn, R. Mehrabian

This work was initiated at the National Bureau of Standards at the request of the National Aeronautics and Space Administration. It was motivated by serious Government and aerospace industry concerns on the possibility that substrength aluminum alloys may have been used in aircraft and space vehicle structures. These concerns originated from the discovery of "soft" spots in an anodized 2024-T851 aluminum alloy machined part in June 1979. The part was machined from a $\sim$ 14 cm (5.5 in.) thick plate of the alloy produced at a particular manufacturing plant. It was postulated that the "soft" spots were due to improper processing of the plate. Furthermore, it was established that the same plant was producing a variety of other aluminum alloy plates including the 2219 aluminum alloy which was the subject of this investigation.

The aim of this work was to develop specific relationships between processing variables used during ingot casting, working, and heat treatment of the alloy, and the resulting microstructures, properties, and NDE responses. This detailed blend of metallurgical examination of the alloy with its NDE response is necessary not only to attack the specific problem at hand but also to gain a fundamental knowledge of the features of metallurgical microstructures which cause changes in NDE parameters.

We have focused primarily on eddy current testing (conductivity) for the present but initial explorations into the use of ultrasonic measurements (wave speed; attenuation) have also been conducted. Work in this program is divided into five areas:

(1) Studies on as-received plate of 2219 aluminum alloy. This is motivated by the realization that the properties vary across plate thickness. These variations can have different effects on various NDE techniques.

(2) Solidification-Segergation Studies. Part of the variation in properties across finished alloy plate is caused by segregation of the alloy components (Cu, Mn) during ingot casting.

(3) Determination of time-temperature transformation diagrams (C-curves) and the relationship between mechanical properties and conductivity. Samples produced during various thermomechanical treatment have a wide range of mechanical properties (hardness, yield strength, tensile strength) and conductivity.

(4) Electron microscopy studies done on the wide range of metallurgical microstructures produced. Extremely fine scale ($\sim$ 100 A) particles are responsible for the strength of aluminum alloys and contribute to associated changes in conductivity.

(5) Predictions of heat flow conditions during malfunctions of the commercial process, namely slow quenching from the solutionizing temperature; and predictions using experimentally determined C-curves of the resultant mechanical property degradations.

Conclusions reached in the study are listed below:

(1) <u>As-received Plate</u>

o Moderate variations in composition, hardness, electrical conductivity, and mechanical properties were noted across the thickness of a 12.7 cm (5 in.) thick 2219 aluminum alloy plate. Composition variations, which influence measured conductivities, can be traced to the original ingot. The variations in hardness and tensile properties are mainly due to changes in cooling rate across the plate during the quench and are probably influenced by inhomogeneous mechanical deformation during processing.

(2) <u>Solidification Segregation Studies</u>

o Macrosegregation of copper in Direct Chill (DC) cast ingots of 2219 aluminum alloy cannot be completely eliminated by chill face scalping and subsequent thermomechanical treatment. Macrosegregation does remain in the finished plate product. However, good scalping practice should limit copper content to above the solid solubility limit with no deterioration in mechanical properties.

- Elements with equilibrium partition coefficients less than unity exhibit macrosegregation similar to copper while those with coefficients greater than unity are opposite to copper. The magnitude of deviations from the nominal are related to the deviation of the coefficient from unity.

- The major phases present in cast 2219 aluminum alloy in this study have been determined by electron microprobe analysis and electron diffraction. They are α-aluminum solid solution, $\Theta CuAl_2$ and Cu_2FeAl_7. These phases are also present in the heat treated finished plate product.

- Predictable macrosegregation has been obtained in laboratory ingots of 2219 aluminum alloy. Both positive and negative segregation similar to DC cast ingots are observed and are caused by the flow of segregated interdendritic liquid. (figure 1)

- Electrical conductivity determined by eddy current measurements of cast 2219 aluminum alloy is inversely related to copper content. This fact complicates the relationship of conductivity to mechanical properties used for nondestructive evaluation of the finished plate product. (figure 1)

- Surface hardness and eddy current measurements may be very sensitive to scalping depth in their ability to evaluate the condition of finished alloy plate.

- Hardness, yield strength, and ultimate tensile strength of heat treated 2219 aluminum alloys decrease significantly when the average copper content drops below approximately 5.5 wt. %.

(3) <u>C-Curve Determination and Relationship between Mechanical Properties</u>

- No significant difference in either strength or hardness was detected between alloys stretched between 5 and 7 percent permanent strain during the thermomechanical processing of 2219 aluminum alloy.

- The functional form developed by Cahn and used previously by Staley for 7075T6 and 6061T6 aluminum alloy was found to give an adequate representation of the C-curves for 2219T87* if the form was modified to include a minimum value for each property in question. Some deficiency in this form at the highest and lowest temperatures was noted.

- An efficient computer program was developed for using time-temperature and property measurement data to establish C-curve parameters.

- For each heat treatment sequence, C-curves were determined for hardness, yield strength, tensile strength, and electrical conductivity. These C-curves can be used to determine the correlations between

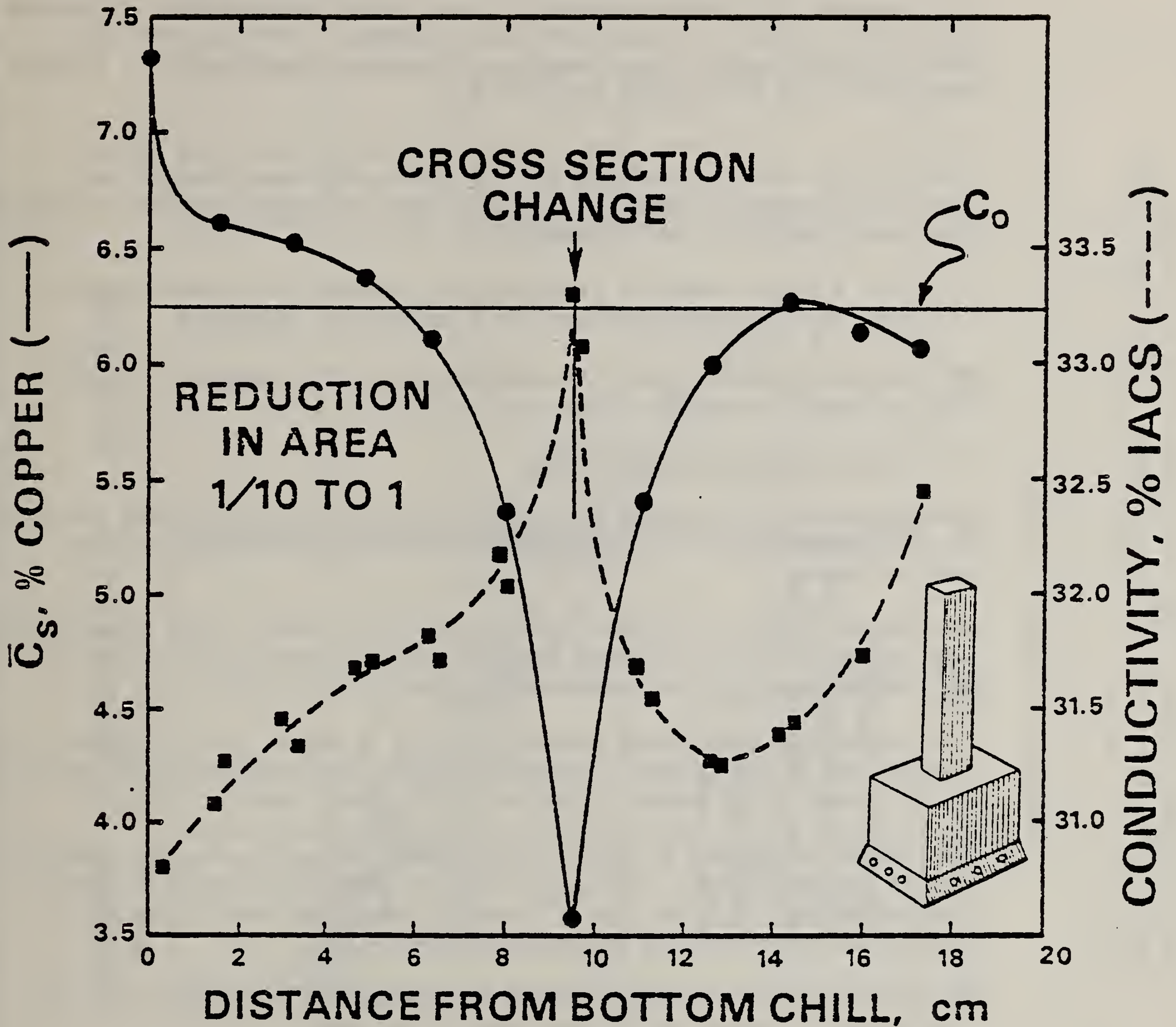


Figure 1. Average copper content and electrical conductivity versus distance from the bottom chill, in a unidirectionally solidified reduced cross section laboratory ingot of 2219 aluminum alloy.

these properties. C-curves could not be developed for elongation, probably because this property is more sensitive to grain size and other factors.

- A small but significant difference was found between the C-curves for sequence A (direct transfer to salt bath) and sequence B (water quench and reheat in salt bath) type quenches. For a given salt bath time and temperature, sequence B quenches resulted in a greater degradation of mechanical properties.

- The scatter in hardness and conductivity was found to be large. This scatter can be expected to complicate NDE measurements and should be properly taken into account when establishing NDE procedures and specifications (see figures 2 and 3).

- There is a great need for standardizing conductivity measurements in order to bring about better interlaboratory agreement.

- 2219 aluminum alloy is not as quench sensitive as some of the other high strength aluminum alloys such as 7050.

(4) Electron Microscopy Studies

- The agehardening response of 2219T87* and T851 is determined principally by the formation of Θ' precipitates with some contribution by Θ" precipitates.

- An abnormal quench treatment which results in dwell times significant with respect to the C-curves leads to the heterogeneous nucleation and rapid growth of Θ and Θ' precipitates.

- The nucleation and growth behavior of the Θ and Θ' precipitates formed during an abnormal quench depend on the preexisting microstructural state of the material and on the thermal "path."

- The large incoherent Θ and Θ' precipitates formed during an abnormal quench consume copper available from the matrix and thereby reduce the concentration of Θ' and Θ" precipitates that contribute to precipitation hardening during subsequent aging.

- The C-curves are a measure of the concentration of large Θ and Θ' precipitates formed during the quench treatment.

(5) Heat Flow Calculations--Property Predictions

- Calculated plate properties, e.g., yield strength and hardness, decrease monotonically with increasing distance from surface to centerline of a plate for fixed heat transfer conditions.

- For symmetric cooling and sequence (a) C-curves, the calculated minimum yield strength (at the center of the plate) is 54.9, 53.7, and 51.8 ksi for 2.54, 7.62, and 12.7 cm (1, 3, and 5 in.) thick plates, respectively.

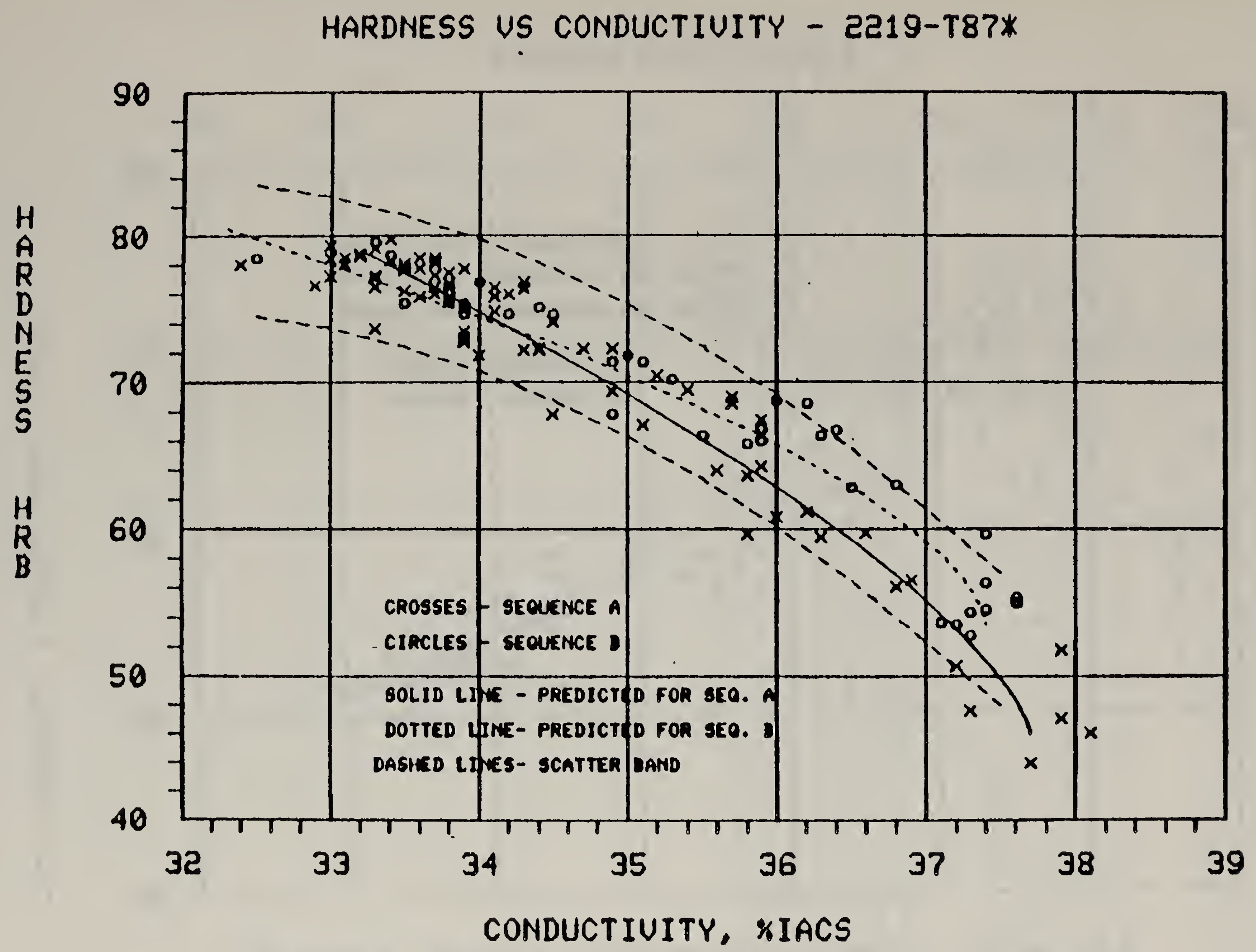


Figure 2. Comparison of hardness vs. conductivity data with the correlations predicted by the C curves. The dashed lines are the scatter band (∿ 95% confidence level) obtained from a least squares quadratic fit to the data.

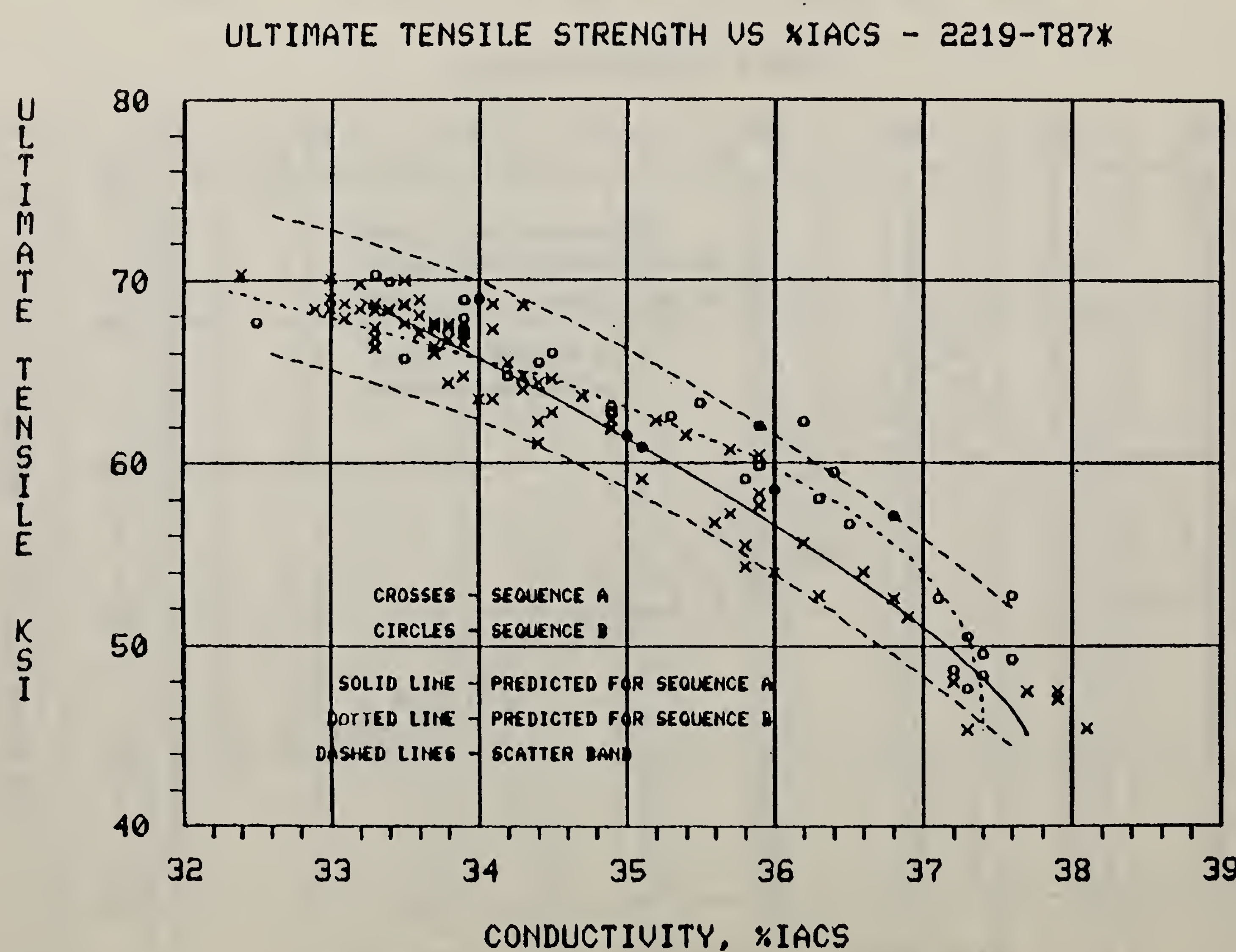


Figure 3. Comparison of tensile strength vs. conductivity data with the correlations predicted by the C curves. The dashed lines are the scatter band (~ 95% confidence level) obtained from a least squares quadratic fit to the data.

- For asymmetric cooling and sequence (A) C-curves, the calculated minimum yield strength (at the bottom surface of the plate) is 54.4, 50.7, 45.9 ksi for 2.54, 7.62, 12.7 cm (1, 3, and 5 in.) thick plates, respectively.

- For plate thicknesses greater than 2.54 cm, sequence (b) C-curves yield lower properties values than sequence (A) C-curves. For example, for asymmetric cooling and sequence (B) C-curves the calculated minimum yield strength is 54.6, 48.0, 41.5 ksi for 2.54, 7.62, and 12.7 cm (1, 3, and 5 in.) thick plates, respectively.

- Interrupted (abnormal) cooling, in which the heat transfer coefficient at the bottom surface changes from the same value as at the top surface to a zero value, can result in lower property values than found for asymmetric cooling. For example, for a 12.7 cm (5 in.) thick plate and sequence (B) C-curves interrupted cooling yields a minimum yield strength of 39.0 ksi compared with 41.5 ksi for asymmetric cooling.

Work in this program will continue in three general areas. A round robin of conductivity measurements at various laboratories has been conducted on NBS-prepared 2219 aluminum alloys in various heat-treated conditions. This work may lead to a set of aluminum alloy conductivity standards. Second, controlled ultrasonic measurements are being planned for pure Al-Cu precipitation hardened alloys. Thirdly, a program has been initiated to investigate the relationship of processing to NDE response of 2024 aluminum alloy. This alloy appears to be more sensitive to heat-treating practice than 2219 aluminum alloy.

Other Activities of the
Metallurgy Division

Invited Talks

The Signal-to-Noise Criterion and Its Implementation as a Generalization of the SVD
International Symposium on Ill Posed Problems: Theory & Practice
University of Delaware, Newark, Delaware
J. A. Simmons and D. F. O'Leary
October 2, 1979

Solid Particle Erosion Mechanisms in Metals
University of Delaware, Newark, Delaware
A. W. Ruff
October 4, 1979

Pin and V-Block and Block-on-Ring Bench Wear Tests for Engine Oil Evaluation
NBS Conference on Measurement Standards for Recycled Oil/Systems Performance and Durability, Washington, DC
L. K. Ives
October 23, 1979

Diffusion and Mass Transport Phenomena in Copper and Copper Alloys
Allegmeine Elektricitats-Gesellschaft, Frankfurt, West Germany
D. B. Butrymowicz
November 12, 1979

Data Evaluation in the NBS Diffusion in Metals Data Center
Academy of Sciences of the USSR, Moscow, USSR
D. B. Butrymowicz
November 14, 1980

Grain Boundary Diffusion
Academy of Sciences of the USSR, Moscow, USSR
D. B. Butrymowicz
November 15, 1979

Diffusion - Induced Grain Boundary Migration
Academy of Sciences of the USSR, Moscow, USSR
D. B. Butrymowicz
November 16, 1979

The NBS Diffusion in Metals Data Center
Academy of Sciences of the USSR, Moscow, USSR
D. B. Butrymowicz
November 20, 1979

Diffusion in Grain Boundaries in Metals
Academy of Sciences of USSR, Kharkov, USSR
D. B. Butrymowicz
November 22, 1979

The NBS Diffusion in Metals Data Center
Academy of Sciences of USSR, Kharkov, USSR
D. B. Butrymowicz
November 23, 1979

Diffusion-Induced Migration of Grain Boundaries in Metals
Academy of Sciences of the USSR, Kharkov, USSR
D. B. Butrymowicz
November 23, 1979

Data Evaluation in the NBS Diffusion in Metals Data Center
Academy of Sciences of the USSR, Kharkov, USSR
D. B. Butrymowicz
November 26, 1979

Numerical Data Evaluation Procedures in the NBS Diffusion in Metals Data Center
Academy of Sciences of the USSR, Kiev, USSR
D. B. Butrymowicz
November 28, 1979

Grain Boundary Diffusion in Metals
Academy of Sciences of the USSR, Kiev, USSR
D. B. Butrymowicz
November 29, 1979

Diffusion-Induced Grain Boundary Migration in Metals
Academy of Sciences of the USSR, Kiev, USSR
D. B. Butrymowicz
November 30, 1979

The NBS Diffusion in Metals Data Center
Academy of Sciences of the USSR, Kiev, USSR
D. B. Butrymowicz
November 30, 1980

Models and Analytic Mechanisms for the Testing of Diffusion Data
Trans Tech SA, Aedermannsdor, Switzerland
D. B. Butrymowicz
December 6, 1979

Corrosion and Fatigue of Surgical Implant Metals
The Johns Hopkins University, Baltimore, Maryland
Anna C. Fraker
February 12, 1980

Reproducible Acoustic Emission by Indentation in Steels
Third International Conference on NDE in the Nuclear Industry,
Salt Lake City, Utah
R. B. Clough and J. A. Simmons
February 13, 1980

Hydrogen Oxidation on Mo-W Carbide Alloy Catalysts
Annual AIME Meeting, Las Vegas, Nevada
A. J. McAlister and L. H. Bennett
February 25, 1980

Solutal Convection Effects
Marshall Space Flight Center, Huntsville, Alabama
W. J. Boettinger
March 5, 1980

Reflection Topography of Subgrain Misorientation
U.S.-France Cooperative Science Program, Paris, France
M. Kuriyama
March 12, 1980

Czochralski Growth of Ni Single Crystals
U.S.-France Cooperative Science Program, Paris, France
M. Kuriyama
March 13, 1980

Oblique Magnetic Domain Walls in Nickel
U.S.-France Cooperative Science Program, Paris, France
M. Kuriyama
March 14, 1980

Surface Tension Measurements of Gallium
Marshall Space Flight Center, Huntsville, Alabama
S. C. Hardy
March 20, 1980

X-Ray Topography: Dynamical Diffraction for Imperfect Crystals
Universitat Dortmund, Dortmund, Germany
M. Kuriyama
March 21, 1980

Interface Stability During Rapid Solidification
Second International Conference on Rapid Solidification Processing,
Reston, Virginia
S. R. Coriell
March 24, 1980

Rapid Solidification Processing--An Outlook
Second International Conference on Rapid Solidification Processing,
Reston, Virginia
R. Mehrabian
March 24, 1980

Mechanisms of Solid Particle Erosion
Engineering Foundation Meeting, Asilomar, California
A. W. Ruff
March 24, 1980

Microstructural Studies of Copper Alloys and Steels After Sliding Wear
Cornell University, Ithaca, New York
A. W. Ruff
April 8, 1980

Materials Processing--A Solidification Processing Perspective of the Field
1980 Burgess Memorial Lecture, ASM, Washington, DC
R. Mehrabian
April 14, 1980

Theory and Experiments in Acoustic Emission
Stanford University, Palo Alto, California
J. A. Simmons
April 15, 1980

Acoustic Emission: Theory and Experiments
Lawrence Livermore Laboratory, Livermore, California
J. A. Simmons
April 17, 1980

Focusing Arrangements and Crystals for Laboratory EXAFS
University of Washington, Seattle, Washington
G. G. Cohen
April 28, 1980

Gating Practice in Die Casting
American Die Casting Institute, Chicago, Illinois
R. Mehrabian
April 31, 1980

Hard Surfacing for Valve Applications
University of Wisconsin, Madison, Wisconsin
K. J. Bhansali
May 20, 1980

A Database for Enthalpies of Formation of Binary Transition Metal Alloys
CALPHAD Conference, Montreal, Canada
L. H. Bennett and R. E. Watson
May 26, 1980

Optimized Predictions for Heats of Formation of Transition Metal Alloys
CALPHAD Conference, Montreal, Canada
R. E. Watson and L. H. Bennett
May 27, 1980

Interactive Computer Graphics for Storing Phase Diagrams
CALPHAD Conference, Montreal, Canada
J. L. Murray and D. J. Orser
May 28, 1980

A New Technique for Calculating Near Field Elastic Wave Propagation in a Plate National Meeting of the Society for Industrial and Applied Mathematics,
Alexandria, Virginia
J. A. Simmons and J. R. Willis
June 5, 1980

Convective and Interfacial Instabilities During Directional Solidification
Twenty-Third COSPAR Conference, Budapest, Hungary
S. R. Coriell
June 9, 1980

Influence of Nickel on Galling Resistance of Cobalt Base Alloys
Gordon Research Conference, New London, New Hampshire
K. J. Bhansali
June 9, 1980

Solid Particle Erosion of Metals and Ceramics: Observations of Sliding Wear Deformation Processes on Steels
Gordon Conference on Friction, Lubrication and Wear, New London, New Hampshire
A. W. Ruff
June 10, 1980

Origin and Characterization of Acoustic Emission in Metals
DARPA Materials Research Council, La Jolla, California
H. Wadley
July 11, 1980

Theory and Experiments on Acoustic Emission
DARPA Materials Research Council, La Jolla, California
J. A. Simmons
July 11, 1980

Theory of Acoustic Emission
DARPA/AFML Review of Progress in Quantitative NDE, La Jolla, California
J. A. Simmons and R. B. Clough
July 14, 1980

Ternary Alloys of Tungsten Carbide for Fuel Catalysts in Acid Fuel Cells
National Fuel Cell Seminar, San Diego, California
A. J. McAlister, L. H. Bennett and M. I. Cohen
July 15, 1980

Low Temperature Heat Capacity of Metallic Glasses
Reactor Radiation Division Meeting, National Bureau of Standards, Washington, DC
R. D. Shull
July 24, 1980

Convective and Interfacial Instabilities During Unidirectional Solidification of a Binary Alloy
Engineering Foundation Conference, Rindge, New Hampshire
S. Coriell
August 7, 1980

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J. A. Simmons and R. B. Clough, Members

E7.04: Joint Task Group on Acoustic Emission; Sensitivity Calibration
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International Journal of Crystal Growth
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International Journal of Diffusion and Defect Data
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Society of Automotive Engineers/American Society of Testing and Materials Unified Numbering System for Metals and Alloys
    J. R. Cuthill, Alternate Representative
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Society of Rheology
    R. Mehrabian, Member

Publications

Rapid Solidification
J. W. Cahn, S. R. Coriell, and W. J. Boettinger
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Consolidation of Plasma-Sprayed Coatings by Laser Remelting
J. D. Ayers and R. J. Schaefer
SPIE, 198, 57-64 (1979)

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R. E. Watson and L. H. Bennett
Phy. Rev. Letters, 43, 1130 (1979)

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R. C. Reno, L. J. Swartzendruber, and L. H. Bennett
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A Study of Deformation and Fracture Processes in a Low-Alloy Steel by Acoustic Emission of Transient Analysis
H. N. G. Wadley and C. B. Scruby
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Eddy-Currents in a Conducting Cylinder with a Crack
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R. B. Clough and J. A. Simmons
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Division Seminars

The Role of Electron Band Theory in the Prediction of Phase Diagrams
R. E. Watson
Brookhaven National Laboratory, Upton, New York
October 24, 1979

Challenges and Opportunities for Nondestructive Inspection Technology in the High Volume Consumer Goods Industries
E. P. Papadakis
Ford Motor Company, Detroit, Michigan
November 19, 1979

A Comparison of Experiment and Theory of Continuous Ordering
H. Chen
University of Illinois at Urbana-Champaign, Urbana, Illinois
December 14, 1979

Comparison of Electron and Laser Surface Melting in the Preparation of Tool Steels
P. Strutt
University of Connecticut, Storrs, Connecticut
January 15, 1980

Effect of Microstructure on Properties of $\alpha + \beta$ Ti Alloys
J. C. Williams
Carnegie-Mellon University, Pittsburgh, Pennsylvania
January 17, 1980

Hydrogen Related Fracture Mechanisms
H. K. Birnbaum
University of Illinois at Urbana-Champaign, Urbana, Illinois
January 23, 1980

Sealing Laws in Solidification
M. E. Glicksman
Rensselaer Polytechnic Institute, Troy, New York
March 7, 1980

Vacancies and Kinetics of Ordering Processes in Alloys
K. Lücke
Institute für Allgemune Metallkunde and Metallphysik, Aachen, West Germany
March 10, 1980

Design and Wear Testing of a Continuous Fiber/Particulate Composite Total Surface Hip Replacement
J. Roberts
Rensselaer Polytechnic Institute, Troy, New York
March 18, 1980

Recent Developments in the State Variable Description of Nonelastic Deformation
M. Jackson
Cornell University, Ithaca, New York
March 19, 1980

VAR--The Vacuum Arc and Metal Transfer
F. J. Zanner
Sandia National Laboratories, Albuquerque, New Mexico
March 21, 1980

Development of Superplastic Microstructures and Microstructure-Property Relations
O. D. Sherby
Stanford University, Stanford, California
March 28, 1980

Analysis of Instability Phenomena During the RF Heating and Melting of Ceramics
R. F. Sekerka
Carnegie-Mellon University, Pittsburgh, Pennsylvania
April 18, 1980

Digital Image Processing, A Personal Account, from SEM to RPV
M. Oron
Stanford University, Stanford, California
April 29, 1980

New Results and Open Mathematical Questions in Modeling the Interactions of Pores and Grain Boundaries in Metals
R. L. Coble
Massachusetts Institute of Technology, Cambridge, Massachusetts
May 21, 1980

Ultrasonic Measurement of Solid/Liquid Interface Position
R. L. Parker
National Bureau of Standards, Washington, DC
May 27, 1980

Ultrasonic Studies of Defects in Irradiated Metals
K. Holtman
University of Illinois, Urbana, Illinois
June 19, 1980

The Use of Positron Annihilation in Metal Physics
S. Berko
Brandeis University, Waltham, Massachusetts
June 17, 1980

Aluminum Rapid Solidification Alloy Processes
W. S. Cebulak
Alcoa Laboratories, Alcoa Center, Pennsylvania
June 19, 1980

A Variational Approach for Waves in Random Composites
J. Willis
Atomic Energy Research Establishment, Harwell, United Kingdom
July 1, 1980

Dual Phase Steels
M. S. Rashid
General Motors Technical Center, Warren, Michigan
July 29, 1980

External Recognition

IR-100 Award on X-ray Magnifiers
1979
W. J. Boettinger, H. C. Burdette, and M. Kuriyama

NBS EEO Annual Individual Award
November 1979
G. J. Mattamal (joint with R. B. Johnson)

Johns Hopkins University Citation
Student Coop Program with NBS
June 1980
G. J. Mattamal

Books

Theory of Alloy Phase Formation
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1980

Rapid Solidification Processing: Principles and Technologies II
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Claitor's Publishing Division, Baton Rouge, Louisiana
1980

Special Reports

NBS: Materials Measurement
J. R. Manning
NBSIR 80-2082

Analysis of Erosion-related Failure Information from Coal Gasification Systems
A. W. Ruff
NBS Report 80-2045

Studies of Microscopic Aspects of Wear Processes in Metals
A. W. Ruff and P. J. Blau
NBS Report 80-2058

Nondestructive Evaluation of Nonuniformities in Aluminum Alloy Plate
L. J. Swartzendruber, L. K. Ives, W. J. Boettinger, R. B. Clough, S. R. Coriell, P. J. Blau, J. W. Cahn, and R. Mehrabian
NBS Special Report to NASA (1980)

Nondestructive Evaluation of Nonuniformities in 2219 Aluminum Alloy Plate--Relationship to Processing
L. J. Swartzendruber, L. K. Ives, W. J. Boettinger, S. R. Coriell, D. B. Ballard, D. E. Laughlin, R. B. Clough, F. S. Biancaniello, P. J. Blau, J. W. Cahn, and R. Mehrabian
Technical Report to National Aeronautics and Space Administration, Washington, DC (1980)

Standard Reference Materials

Supplied Office of Standard Reference Materials with 150 units of SRM-469 and issued 54 units of SRM-484.

An electron microprobe standard reference material (Fe-Cr-Ni alloy) was produced by F. S. Biancaniello, P. A. Boyer, and A. W. Ruff of the Metallurgy Division cooperatively with the Center for Analytical Chemistry. This SRM represents a composition standard used on the micrometer scale of homogeneity in many analytical laboratories in the U.S. and abroad. The first production lot of this SRM was sold out requiring the production and certification of a second lot of material.

Patents

Acoustic Embrittlement Detector
R. B. Clough and R. Fields
NBS Cast No. 1845
August 5, 1980

Nickel Base Wear Resistant Alloy
K. J. Bhansali
January 1, 1980
U.S. Patent 4,181,523

Sponsored Conferences

Measurement and Standards for Recycled Oil/Systems Performance and Durability
NBS, Gaithersburg, Maryland
October 23-26, 1979
A. W. Ruff, Co-Chairman

Second International Conference on Rapid Solidification Processing: Principles and Technologies
Reston, Virginia
March 23-26, 1980
R. Mehrabian, Chairman

Failure Prevention in Ground Transportation System
NBS, Gaithersburg, Maryland
April 22-24, 1980
A. W. Ruff, Organizing Committee

Implant Retrieval: Material and Biological Analysis
NBS, Gaithersburg, Maryland
May 1-3, 1980
A. W. Ruff, Co-Chairman
A. C. Fraker, Organizing Committee

CERAMICS, GLASS, AND SOLID STATE SCIENCE DIVISION

CERAMICS, GLASS, AND SOLID STATE SCIENCE DIVISION (565)

Hans P. R. Frederikse, Chief
Stanley Block, Deputy Chief
B. A. Hyde, Secretary
M. A. Clevinger, Secretary
J. Bartlett,Secretary
E. R. Smith, Secretary
K. R. Morgan, Secretary

This Division is devoted to research that emphasizes several categories of technologically important materials: ceramics, glass, and optical materials. It employs a number of broad disciplines: crystallography, solid state chemistry, and solid state physics. The nature of the work is both applied and fundamental. The results of this work are new measurement techniques, reference data, and standard reference materials as well as improved understanding of the structure and properties of solids. The output is widely used in the ceramic, glass, and optical industries both in processing, design, and lifetime assessment of devices, components, and structures.

The present activities of the Division are organized in four Tasks:

12151	STRUCTURAL CHEMISTRY FOR CERAMIC PROCESSING AND DURABILITY
12153	STRUCTURAL METHODS FOR PROCESSING, MANUFACTURING, AND DURABILITY
12154	PROPERTIES, STRUCTURE AND STANDARDS FOR GLASS AND OPTICAL MATERIALS
12155	DURABILITY OF CERAMICS AND GLASS IN SERVICE ENVIRONMENTS

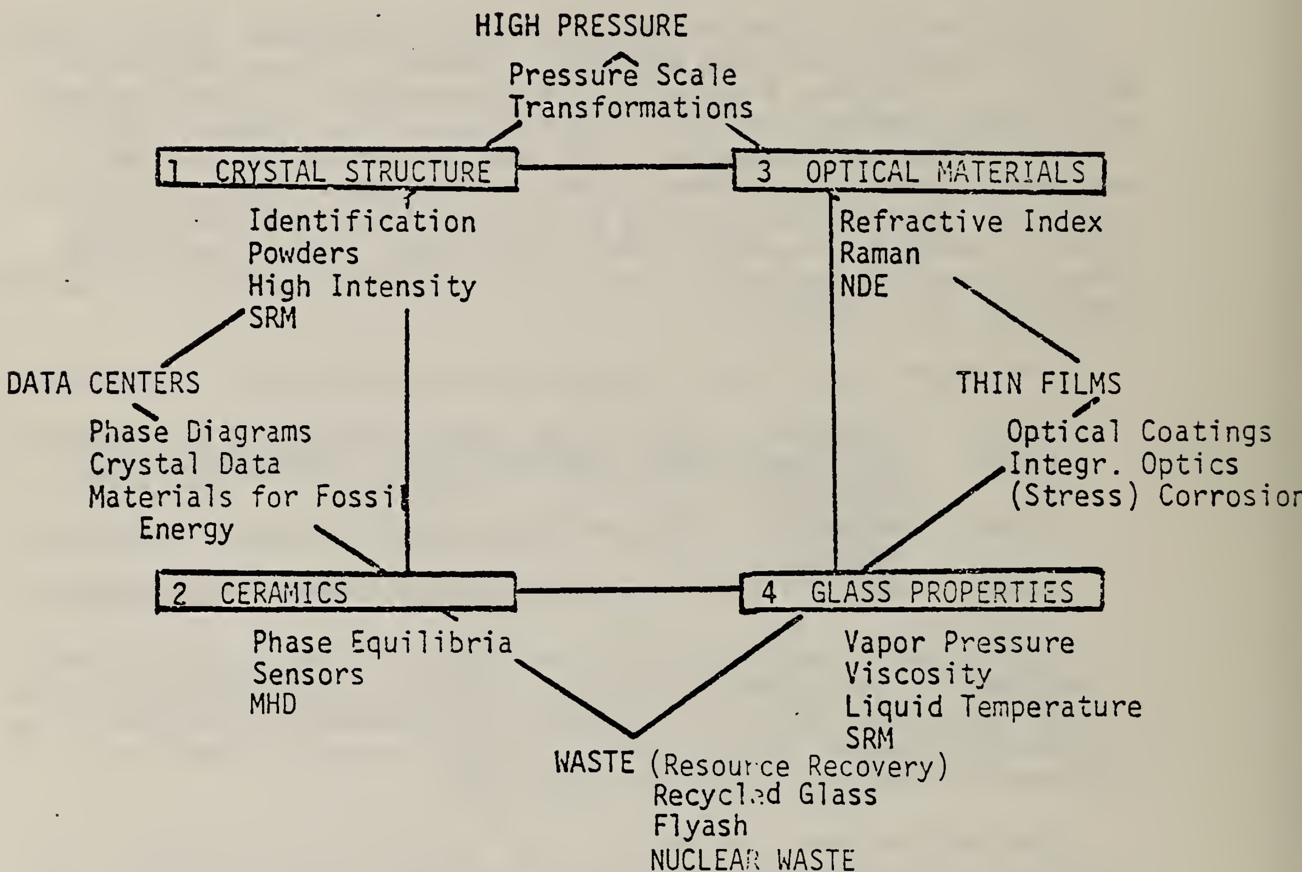
Another way to explain the various aspects of the Division's work is depicted in the diagram of figure 1. Basically the Division consists of four groups with several overlapping and cooperative activities. The collaboration extends to many other Divisions, research teams, and individual scientists inside and outside NBS.

The Division sees three major trends governing the direction of the science and technology during the next few years, and consequently the program is shaped accordingly. These three trends are:

1. Higher Temperatures and Pressures

An example of a technological development in this area is the work of the Division on fluidic capillary pyrometers for the measurement of temperatures (and oxygen partial pressures) in extreme environments. This work is performed together with the Harry Diamond Laboratories (U.S. Army) and the Trans Tech Corporation (Gaithersburg, MD), a cooperative effort that has produced considerable interest from several large and small industrial companies.

Figure 1. CERAMICS, GLASS, AND SOLID STATE SCIENCE DIVISION



Development of and research with the diamond anvil pressure cell is one of the most important projects in the Division aimed both at scientific and technological applications. NBS receives nearly daily requests for information about the high pressure technique and research results from researchers in the U.S. and abroad.

2. Small Dimensions

There is an ever-increasing interest in thin films, small particles, and crystalline grains with dimensions of 1 nm to 1 μm. The emphasis is on measurement techniques for the determination of composition and properties of these small-dimension materials both for technical applications (communication, optics, corrosion and protection, powder processing, and manufacturing, etc.), and for scientific understanding (differences and similarities of films or particles and bulk material).

A little more than a year ago the Division initiated a project concerned with the production and characterization of glassy thin films. This thin film facility, consisting of a deposition and a characterization chamber has been in operation since early 1980. Glassy thin films to be used as antireflection coatings for large glass lasers have been produced. Other work is concerned with oxide layers formed on metals and with the mechanism of cracking under stress.

3. Automation and Computerization of Data Acquisition, Storage and Retrieval

Both the Crystal Data and Powder Diffraction projects have put considerable emphasis on the automation of data acquisition through minicomputer control and on the development of programs for data analysis, evaluation, and dissemination.

Other activities that have benefited from equipment automation and computerized data handling are the Raman project, Scanning Electron Microscopy, the Fossil Energy Materials Data Center, the Thin Film Facility, the High Pressure Research, the Phase Diagram for Ceramists Program, and the acquisition of electrochemical materials data.

During this year the Division has been involved in the planning of a number of programs for possible future implementation. In this context we should mention the programs on Powder Processing for High Performance Ceramics and on Glass Ceramics. Together with other Divisions of CMS, plans were also developed in the areas of Mass and Charge Transport and work on high pressure research on lubricants was suggested in the framework of the Tribology program.

Other possible programs in the early planning stage including those in the areas of Thin Films, Amorphous Materials, and Tribology.

The Optical Materials Projects of the Division received considerable visibility through the organization of a Topical Conference on Basic Optical Properties of Materials held at NBS, May 5-7, 1980.

The Division will benefit much from the training received by Dr. R. S. Roth who spent three months at Arizona State University familiarizing himself with the high resolution electron microscope and performing some highly interesting research on lattice imaging of several ceramic compounds.

STRUCTURAL CHEMISTRY FOR CERAMIC PROCESSING AND DURABILITY
Task 12151

The major goals of this task are:

to provide methods and obtain data for the construction and evaluation of phase diagrams of systems containing oxides, sulfides, oxynitrides, etc. Attention will be focused on silicates with additions of one to six other oxides, which form the basis of the very important (coal) slags;

to study the composition, phases, and properties of various oxide systems with either random or ordered defects or partly-ordered (modulated) structures and to unravel the relation between the charge transport and nonstoichiometry of these compounds; and

to assess the potential of ceramics and related materials for use in energy conversion devices, for catalyzing chemical processes, and for storing both beneficial and harmful elements and compounds.

As these goals are very broad it is necessary to be more specific in the subtasks under investigation. The materials actually examined in the course of this study can be divided into two groups. The first group consists of the seven most abundant oxides in the earth's crust which make up the composition of coal slag and of most high volume refractory ceramic materials (Na_2O, K_2O, CaO, MgO, FeO_x, Al_2O_3, SiO_2). The second group consists of materials of interest in high technology ceramics, for electronics, electrodes, catalysts, ionic conductors, dielectrics, etc.

The experimental determination of complex phase equilibria in a multicomponent system is a very laborious and time-consuming effort. Therefore, we are seriously examining existing computer programs for prediction of phase equilibria from thermochemical data. We hope eventually to be able to modify such programs to be useful for the prediction of solid-solid and solid-liquid equilibria in complex systems of interest to the ceramic industry.

During the last several years and especially since July 1974, as a response to the national need, much of the work has been directed to the area of materials research for energy conversion. Most staff members in the task are now working directly on materials problems in several energy-related disciplines, for example ceramics for magnetohydrodynamic (MHD), gas turbines, batteries, and fuel cells. At the request of DOE, members of the task have begun several new projects, one on ceramics for high temperature structural use in gas turbines, etc., such as Si_3N_4 and SiC based materials and another program on the possible use of ceramics as hosts for nuclear waste storage.

R. S. Roth spent three months at Arizona State University, collaborating with the staff members of that facility's Center for Solid State Science on the use of high resolution electron microscope lattice images to elucidate the nature of chemical reactions in specimens previously prepared at NBS, and as a learning process to make it possible for 12151 task personnel to utilize the new STEM facility now being set up in the Center for Materials Science.

Phase Diagrams for Ceramists
Subtask 1 of Task 12151

L. P. Cook, T. Negas, R. S. Roth (M. A. McKenna and J. T. Fitzgerald)

Within the last year it has become necessary, because of the size of the final publication, to prepare as two volumes the 1980 supplement to "Phase Diagrams for Ceramists." Numbering of these volumes will be such that the 1964, 1969, and 1975 editions are treated as Volumes 1-3 and so these new supplements will be Volumes 4 and 5. It is anticipated that they will be roughly the size of the previous volumes. Volume 4 will contain figures 5000-5590 (metal-oxygen, metal oxides, and oxygen-containing radicals). Due to the fact that many figure numbers actually represent more than one diagram, Volume 4 will actually contain 748 phase diagrams of oxide systems and 90 diagrams involving oxygen-containing radicals or 838 diagrams in all. Volume 5 will contain figures 5591-6345 (molten salts, sulfides, oxycarbides, and oxynitrides, aqueous systems, and ceramic/gas systems), with a total of 987 diagrams, as well as the cumulative indexes, provided size limitations are not exceeded. The American Ceramic Society has decided to publish this volume with in-house computer assisted typesetting. Proofs of the diagrams and many of the commentaries have already been received and Volume 4 is scheduled to be published in late 1980. Volume 5 will probably be published in 1981.

The use of computer methods is continuing to increase in the preparation of the compilation. Chemical arrangement of the book and preparation of contents, chemical indexes, and author indexes is now done with a computer. With the aid of a summer student and a computer scientist these procedures as well as the editing procedures are being streamlined.

In addition, under a new program for centralization of OSRD-sponsored activities, the Phase Diagrams for Ceramists Data Center is collaborating with the other NBS data centers in the development of common data formats to allow the data centers to interact more efficiently and to allow the development of generalized software for NBS data base management. It is hoped in the future that all aspects of the compilation preparation will make use of, insofar as possible, computerized file management. Although the amount of time required initially for conversion to this type of system is substantial, the outcome should allow more efficient use of the limited number of personnel available for the Phase Diagrams for Ceramists project.

An attempt is currently being made to evaluate published methods of calculating phase equilibria diagrams and to find appropriate models to obtain better fit between calculation and experimental data. Development of the quasichemical silicate melt polymerization model begun last year continued. The effect of varying oxygen partial pressure on the predicted high temperature two liquid field in the system K_2O-CaO-MgO-FeO_x-Al_2O_3-SiO_2 was examined by successive calculation of free energy mixing curves for Fe^{+3}/Fe^{tot} of from 0.05 to 0.30. A rather dramatic effect was observed--

the predicted tendency for unmixing is almost negligible under reducing conditions but becomes very great under oxidizing conditions. These predictions will be tested experimentally.

Further development of the quasichemical model to the point where liquidus surfaces can be reasonably well predicted for a range of multicomponent melts is being attempted in the system K_2O-CaO-Al_2O_3-SiO_2. This is a system where a variety of melt structures might be expected, yet there are sufficient thermochemical data and phase equilibrium data such that a detailed analysis of melting curves can be carried out in order to test polymerization theories. In practice this is done by comparison with ideal solution curves. The greatest difficulty comes in explaining the effect of Al_2O_3 and it may be that the quasichemical model will have to be appreciably modified to accommodate alumina-rich compositions.

Ceramic Ion Conductors and Capacitors
Subtask 2 of Task 12151

R. S. Roth, H. S. Parker, T. Negas (L. C. Martel and M. C. Austin)

The following ongoing projects are being conducted in collaboration with scientists of other organizations and other Divisions at NBS, on the phase equilibria and crystal chemistry of ceramics of interest for their ordered defect structures, "tunnels," layers, or three-dimensional continuous defect arrays with possible applications for oxygen, Li-, Na-transport, in batteries, etc.

Scheelite-Related Phases--Several systems containing rare earths and niobium or tantalum oxide were studied in previous years in an attempt to elucidate the crystal chemistry of oxygen excess structures related to $CeTaO_4$ and $CeNbO_4$. During the course of the present year the phase equilibrium diagrams of the systems $LaNbO_4$-$ThNbO_{4.5}$ and $LaNbO_4$-$LaWO_{4.5}$ were completed (figure 1). Several manuscripts were prepared by R. J. Cava, now with Bell Telephone Laboratories, and members of this group.

A group of compositions from these two systems were carried to Arizona State University for study by high resolution electron microscopy. In a collaborative study with Dr. A. Olsen of Arizona State University the incommensurate nature of these materials was clearly demonstrated. A material can be said to have an incommensurate structure when the diffraction pattern cannot be explained on the basis of a small whole number superstructure but instead has an irrational value to the multiple diffraction effects. The electron diffraction patterns and their corresponding high resolution lattice images demonstrated that these phases were incommensurate (figure 2). A manuscript has been prepared by A. Olsen and R. S. Roth on the incommensurate superstructures in these systems.

Neutron diffraction total profile analyses have been conducted on the monoclinic $CeNbO_4$, $CeTaO_4$, and $NdTaO_4$ structures as well as the high temperature orthorhombic $LaTaO_4$ phase. New mathematical treatments are currently being devised by A. Santoro of the Reactor Division in an attempt to treat the structures of the incommensurate modulated phases of

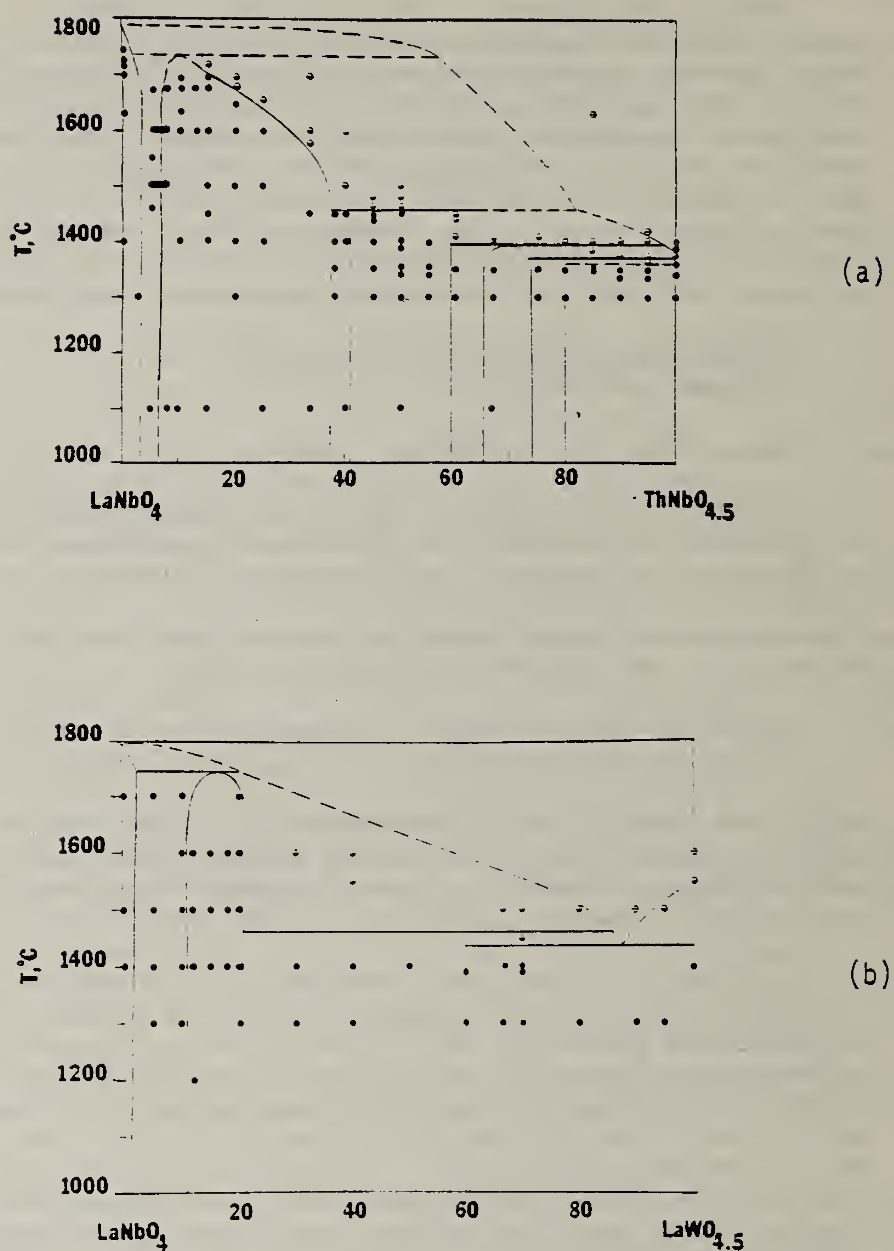


Figure 1. Phase equilibria diagrams of the systems:
(a) $LaNbO_4$-$ThNbO_{4.5}$ (b) $LaNbO_4$-$LaWO_{4.5}$.

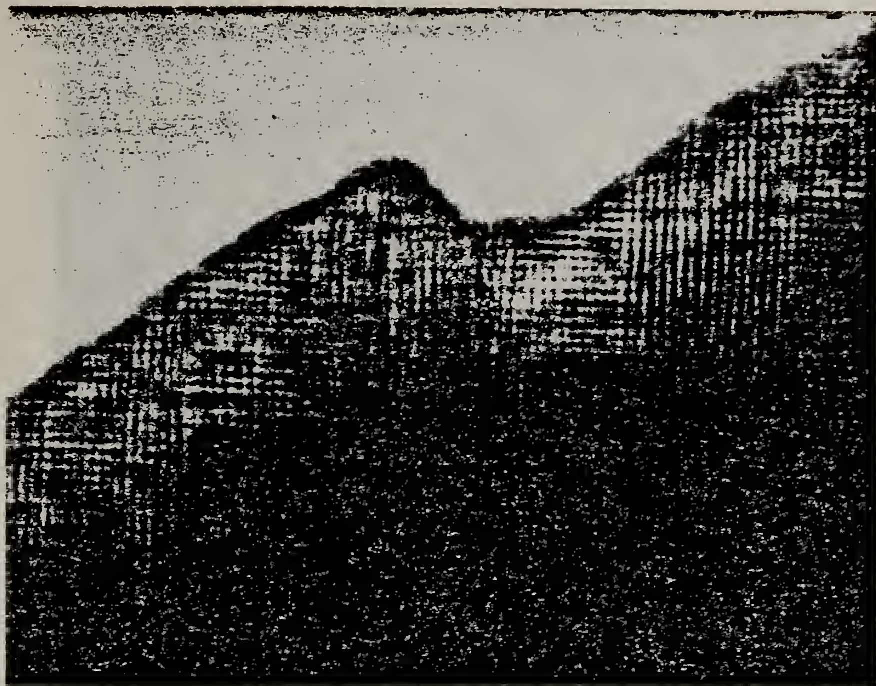


Figure 2a. Bright field lattice image of $La_{.9}Th_{.1}NbO_{4.05}$.

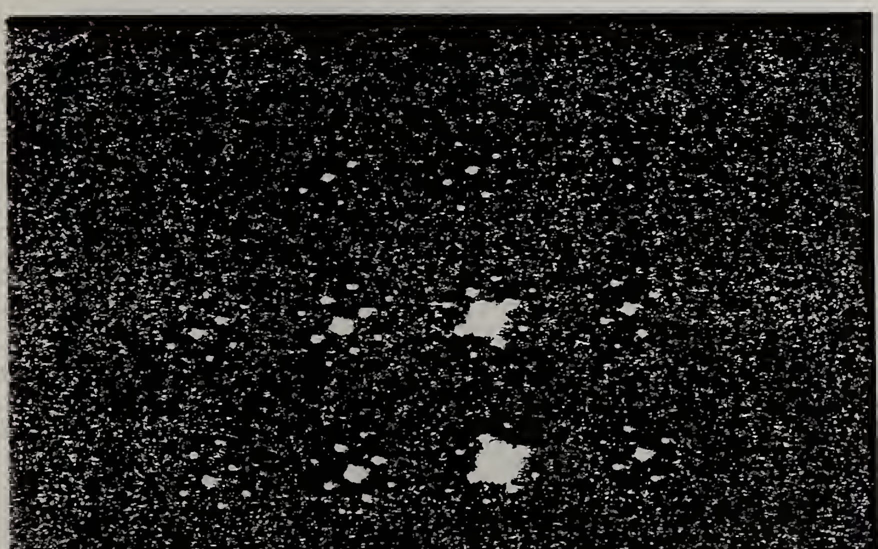


Figure 2b. Electron diffraction pattern of $La_{.67}Th_{.33}NbO_{4.166}$.

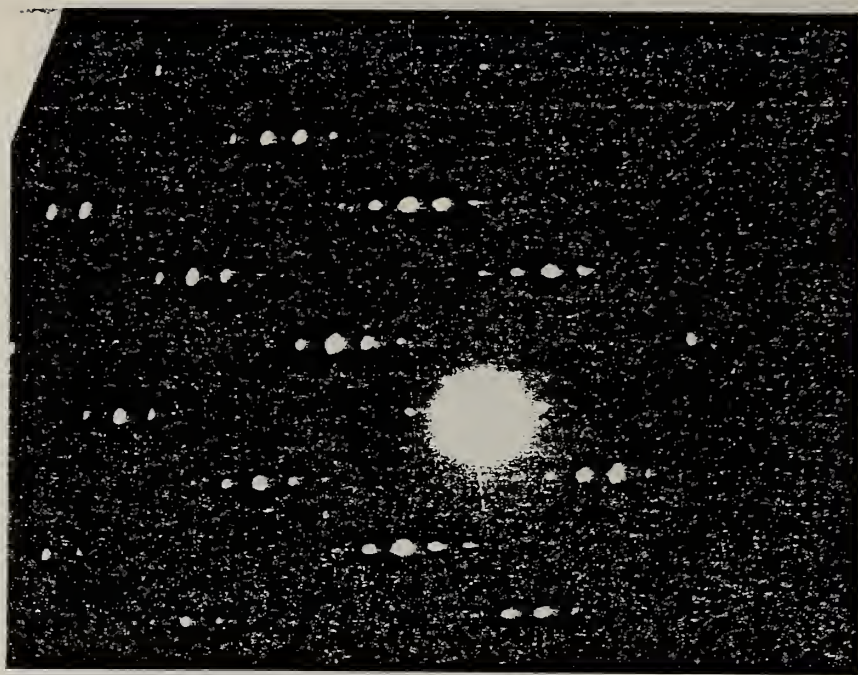


Figure 2c. Electron diffraction pattern of $La_{.55}Th_{.45}NbO_{4.225}$.

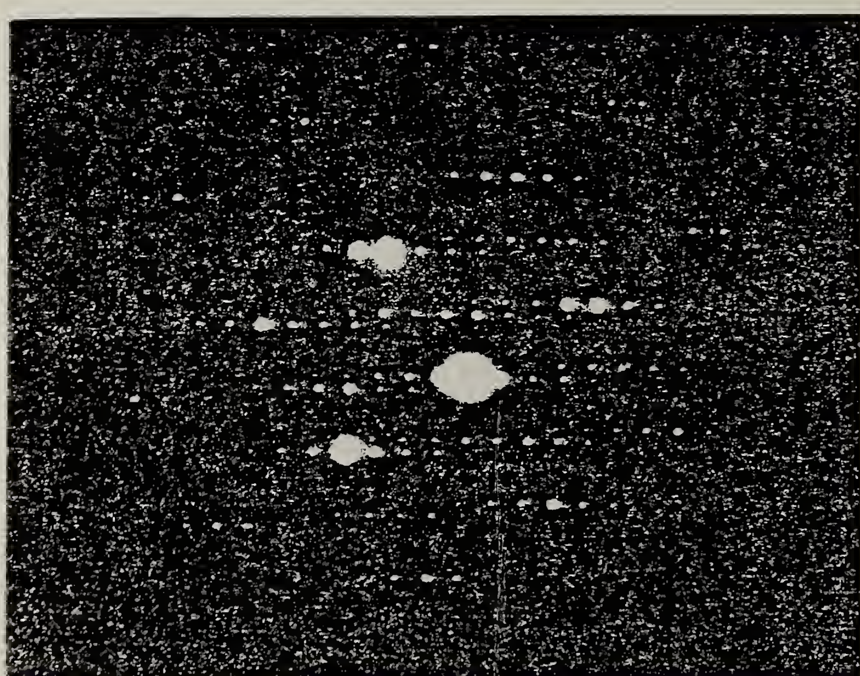


Figure 2d. Electron diffraction pattern of $La_{.33}Th_{.67}NbO_{4.33}$.

$CeTaO_{4+x}$ and $CeNbO_{4+x}$. These structures are currently being examined on specimens supplied by NBS, using single crystal x-ray diffraction techniques, by Dr. M. Marezio of the University of Grenoble, France.

Titanates--The phase equilibria and crystal chemistry of a portion of the system BaO-Nd_2O_3-TiO_2 is currently being studied in a collaborative project with Dr. D. Kolar of Josef Stefan Institute, Ljubljana, Yugoslavia, as part of a joint U.S.-Yugoslav agreement. Several compositions in this system are being used in Yugoslavia in electronic components for their property of high dielectric constant with low temperature coefficient of the dielectric constant. Small single crystals of three new compounds were prepared at NBS during the course of the phase equilibria study. A paper authored jointly by Yugoslav and NBS scientists has been submitted for publication. It contains indexed powder patterns and unit cell dimensions of the three phases, $BaNd_2Ti_3O_{10}$ (1:1:3), $BaNd_2Ti_5O_{14}$ (1:1:5), and $Nd_4Ti_9O_{24}$ (4:9).

Several compositions from this ternary system prepared at NBS were carried to Arizona State University for examination by electron diffraction and high resolution lattice images. It was not too difficult for Dr. A. Olsen of Arizona State to arrive at trial structures for the 1:1:5 and 1:1:3 compounds. A manuscript has been prepared by A. Olsen and R. S. Roth on a crystal structure model of $BaNd_2Ti_3O_{10}$ from high resolution microscopy. Electron diffraction shows that the true unit cell of this phase is monoclinic rather than orthorhombic. Calculated lattice images correspond well with the observed images when using the proposed structure based on neodymium titanate perovskite units three octahedra wide separated by layers of Ba^{+2} ions. The lattice image of the 1:1:5 phase cannot be uniquely interpreted without high resolution data which can be obtained on the new JEOL 200 CX instrument being installed at Arizona State. Similar studies could probably be made with the Phillips 400 microscope recently purchased by NBS, CMS.

Li_2O-Containing Phases--In an ongoing collaborative study with Dr. A. Santoro of the Reactor Division several phases are being examined to determine the role of lithium in oxide structures, especially in those of possible interest as lithium ion conductors. We have so far examined and published results of studies of $LiNb_3O_8$ and M-$LiTa_3O_8$ as well as Ta_2WO_8 (with all Li position vacant). The structure of H-$LiTa_3O_8$ has been studied in collaboration with M. Marezio at Grenoble. The structure of the ramsdellite form of lithium titanate with a composition about 1:3 to 6:17 Li_2O:TiO_2 has also been studied in collaboration with Dr. J. Mikkelsen of Xerox Corp. using specimens prepared at NBS and at Xerox.

In an effort to obtain a better understanding of the nature of the difficulty in locating Li^+ ions in oxide structures, several new series of phases are being prepared for study by total profile neutron diffraction powder analyses. The other compounds in the Li_2O-Ta_2O_5 system are being prepared as well as the phases in the systems Li_2O-ZrO_2 and Li_2O-SnO_2 and nonstoichiometric solid solutions between them and the lithium tantalates. Another phase under study is the nonstoichiometric lithium-lanthanum molybdate with scheelite structure.

A new collaborative study has begun with Drs. R. J. Cava and D. Murphy of Bell Telephone Laboratories, Dr. A. Santoro of the Reactor Division, and R. S. Roth of this Division. Dr. Cava is currently an official guest worker jointly with the Ceramics, Glass, and Solid State Science Division and the Reactor Division. This study involves neutron diffraction total profile analyses of Li-intercalated compounds. This study differs from all the other compounds prepared for this program at NBS by utilizing a unqiue room temperature preparative technique instead of high temperature techniques. The resulting materials are thus non-equilibrium phases and are apparently greatly stressed, complicating the structural analyses. The intercalated compounds currently under study include Li_2ReO_3, $LiReO_3$, $Li_2V_2O_5$, and LiV_2O_5. The structures of the rhenium compounds are essentially solved but the vanadium compounds are more difficult and the structure of V_2O_5 itself will be refined first to obtain a greater insight into the problems.

<u>Crystal Growth, Synthesis and Characterization</u>
Subtask 3 of Task 12151

H. S. Parker, W. S. Brower, L. P. Cook, T. Negas (C. D. Olson)

The synthesis and crystal growth of phases in support of NBS materials research programs and collaborative programs with other research laboratories on a national and international scale has continued. Where necessary and appropriate, limited phase equilibrium studies were conducted to aid in the delineation of stability fields and compositional limits. In addition to supportive work for other programs in this task, crystals of AgI have been grown by a solution technique for ionic conductivity studies in collaboration with R. J. Cava of the Bell Telephone Laboratories. Currently the same technique is being used in an attempt to grow crystals of CuI for similar measurements.

A project on corrosive reactions in oxides has been terminated during this year. The objectives of this study, conducted by H. S. Parker and C. D. Olson, with NASA support, were to examine the nature and extent of sample-container reaction up to and including liquidus temperatures and to provide phase equilibria data of interest in the study of slag-electrode reactions in MHD systems. A further objective was to consider alternate techniques for containerless processing.

The initial work on the $KFeO_2$-Fe_2O_3 portion of the study was extended to include selected compositions in the K_2O-FeO-Fe_2O_3-SiO_2 system, studied at controlled partial pressures of oxygen. In contrast to the earlier work with compositions containing Fe_2O_3 where chemical corrosion of platinum was found to be minimal at temperatures as high as 1600 °C, severe reaction with platinum was found as the amount of Fe^{+2} in the specimens increased. The volatility of potassium in this system remains a problem during heating at high temperatures.

The possibility of electromagnetic positioning of selected ceramic oxides having good electrical conductivity at low temperatures (100 ° to 300 °C) during low gravity experiments in space was explored with NASA and other NASA contractors. The collaborative effort with NASA Marshall

Space Flight Center indicated that although suitable for low gravity experiments in space, acoustic levitation and positioning could not be achieved at useful temperatures in a one-gravity environment.

The scanning electron microscope remains an essential piece of equipment for phase equilibrium-related activities. Examples from the past year include: detection and compositional determination of invariant melts in the system K_2O-CaO-Al_2O_3-SiO_2 for comparison with theory; the study of interfacially controlled phenomena in the system K_2CO_3-$KAlO_2$, including the detection of possible mesomorphic behavior and the imaging of what may be long-period crystalline structures; the study of K_2CO_3, K_2SO_4/steel interaction in MHD downstream corrosion simulation experiments; the study of Si_3N_4 sintering and reaction.

In cooperation with the surface microanalysis group at NBS, currently available software for data reduction on energy dispersive x-ray spectra is being adapted to the system. This will allow spectrum stripping and peak deconvolution for easier identification of spectral features and quantitative analysis, including the light element data collected with the windowless system.

Materials for Fluidic Capillary Pyrometer Temperature Sensors
Subtask 4 of Task 12151

T. Negas, H. S. Parker, W. S. Brower (L. P. Domingues)

This subtask in collaboration with Harry Diamond Laboratory (HDL), has been concerned, with developing new techniques of measuring temperature and oxygen partial pressure simultaneously in extreme environments under actual industrial use conditions. In principle, a fluidic capillary pyrometer (FCP) is analogous to an electronic resistance thermometer. The fluid resistance of a capillary is directly proportional to viscosity which, in turn, is a function of temperature. Laminar fluidic pressure amplifiers are utilized to amplify small pressure signals to usable outputs which may be detected by a pressure gauge or transducer. Having constructed some "first-generation" fluidic temperature measurement circuitry, HDL researchers turned their attention to the actual contact temperature sensor or capillary probe. It soon became clear to this group that they needed expert advice with respect to the materials problems related to the high temperature development of such a sensor. In July 1979 the HDL group contacted T. Negas at NBS and discussed with him the various requirements and possible solutions. This association developed into close collaboration when a hybrid fluidic temperature-oxygen concentration sensor was developed jointly by NBS and HDL groups (A Hybrid Fluidic Temperature-Oxygen Sensor, Fall Meeting Electronics Division, American Ceramic Society, Williamsburg, Virginia, October 1979). Subsequently, funding from and cooperation with HDL researchers has increased progressively.

Initially, the HDL group requested ceramic oxide-based sensors of specific design: a double-bore rod (0.25 in. dia. each bore) with a capillary (~ 1-1.5 in. length, 0.030 in. dia.) connecting the two channels at one closed end. In cooperation with Trans Tech., a small specialty ceramics company (represented by L. P. Domingues, now an official guest worker with the Ceramics, Glass, and Solid State Science Division), research culminated in the production of these sensors constructed from alumina, zirconia:Y_2O_3, and spinel ($MgAl_2O_4$). The zirconia-based sensors are transformation toughened materials. Probes up to 24" in length were provided. Several of these sensors were installed in U.S. Army forging furnaces at Scranton, Pennsylvania. These continue to function (~ 6 months) and are destined to be interfaced with existing furnace controls.

More recently, work at NBS has expanded to (a) develop new designs for FCP sensors, (b) develop and/or select construction materials for FCP sensors for specific applicatons, (c) fabricate FCP sensors in cooperation with private industry, (d) provide calibration (not certified) of sensors in the 1000° to 2400 °C range, and (e) test durability of sensors within environments simulating specific applications.

Ceramic, oxide-based sensors having unique, monolithic construction were designed and fabricated. Alumina sensors (24" length) were fabricated to include four internal bores (0.25" dia.), one pair being linked by a capillary while the other pair terminates within the region of the capillary at the closed, sensing portion of the probe. Other improvements in sensor design are under investigation to enhance response time and to simplify processing.

Oxide coated metals and carbides are obvious candidate materials for FCP sensors for certain applications. Their high thermal conductivity ensures rapid response of the probe and contributes to high resistance to thermal stress. As this task has focused on materials for applications well above 1200 °C in various environments, only the refractory metals (e.g., Mo, W, Ta, Zr) and graphite have been considered.

Graphite sensors were designed and fabricated from commercial, high purity, and high density materials. A unique design was established at NBS and successfully tested to 2400 °C. Rather than using a capillary, a porous, permeable graphite plug was used as the fluid resistor within the sensor. Argon was used as the working fluid.

Ceramic coated molybdenum sensors also were constructed to operate within oxidizing or reducing environments. Emphasis was placed on long duration (~ 6-8 hrs) temperature measurements within molten iron and/or steel in the presence of RF and/or high electric fields. Molybdenum sensors were protected against oxidation by several coatings using combinations of cermets and oxides. In cooperation with another private company, APS Materials, these coatings were applied by arc plasma spray (APS) methods. Preliminary testing at NBS and at the General Motors Research Labs, Warren, Michigan, demonstrated that the coated Mo-sensors will survive the thermal shock associated with rapid immersion into molten iron at 1200 and at 1500 °C. One probe operated nearly six hours in molten iron with cycling between 1200 to 1500 °C (note that conventional practice is to use disposable thermocouples, ~ 15 s lifetime). Failure of the protective oxide-based coatings on Mo, in all cases, is at the molten iron-air-slag interface especially at temperatures above ~ 1400 °C. Recent experiments (1500 °C, 7 hrs) indicate that corrosion at this interface can be controlled by sacrificial materials (e.g., castables) around the sensor to extend the lifetime of the oxide-based coatings.

Four-bore alumina FCP temperature sensors were installed within a periodic kiln at a private ceramic firm for the purpose of measuring firing temperatures up to ~ 1600 °C in air. The fluidic measurement circuitry (not the FCP sensor) became unstable due to rapid ambient room temperature fluctuations resulting from large cooling fans. NBS determined that the cause could be attributed to pressure fluctuations which propagate through the system at sound velocity and HDL improved the circuitry and insulated the copper tubing which transports air to and from the sensor to solve the problem.

During this year, HDL and NBS demonstrated that temperature can be measured accurately by fluidics technology combined with appropriate materials and design for a FCP sensor. This technology is competitive with other temperature measurement methods when costs are compared. For example, the protective sheath for a Pt/Rh- and/or W/Re-based thermocouple can obtain the same measurement without the expensive wire. In some applications, the FCP sensor may be the only means by which an accurate contact temperature measurement can be performed. The following laboratories have expressed active interest in utilizing some form of the new sensors: Dupont, General Motors, Kaiser Corp., Electro-nite, Inc., Union Carbide, APS Materials, Argonne National Laboratory, Oak Ridge National Laboratory, U.S. Steel, Acurex Corp., Sandia Labs., Kennecott Corp.

In cooperation with three private firms, highly efficient sprayable powders of alumina-chromia solid solutions are also under development. Coatings of chrome oxide (Cr_2O_3) and aluminum oxide (Al_2O_3) by arc plasma spray (APS) are used extensively in the chemical processing and textile industries due to their hardness and resistance to corrosion. Available alumina powders deposit on substrates as metastable (γ, θ, etc.) forms. Utilization of Cr_2O_3 coatings for resistance to corrosion above ~ 700 to 800 °C results in extensive fissuring due to undetermined factors. Pure alumina coatings fail because of volume changes associated with transition of metastable forms to α-alumina above 1400 °C. Alumina powders, containing ten and twenty weight percent chromia in solid solutions, were processed and efficiently (>> 80 percent) sprayed by APS. For both compositions, a nearly equal mixture of metastable aluminas and α-alumina solid solution products were deposited. To our knowledge this is the first time that α-alumina has been deposited by APS. Coatings are dense (> 90 percent of theoretical) and do not fissure or spall up to 1200 °C on rolled steel. In contrast, pure alumina coatings delaminate under similar conditions. Future work will include testing of these coatings above 1200 °C using Mo-metal substrates.

Nuclear Waste Management
Subtask 5 of Task 12151

T. Negas, R. S. Roth

This project is part of a recently initiated DOE program on waste forms of ceramics and glass. It will include waste forms, measurement techniques, "standard materials," and leaching studies. During 1979-1980, the following visits and conferences were attended by T. Negas to obtain technical insights for the NBS program proposed to DOE: (1) Oak Ridge National Laboratory; (2) Savannah River Laboratories; (3) Idaho Falls National Laboratory; (4) Nuclear Regulatory Commission review of the Department of Energy nuclear waste management program (February 1980), and (5) "Scientific Basis for Nuclear Waste Management," Materials Research Society, Boston, Massachusetts, November 1979.

Additionally, numerous internal technical and administrative meetings were attended to help formulate the NBS policy and program for nuclear waste management through DOE. A significant part of Chapter II, Technical Issues (Nuclear Waste Management document from NBS to DOE), was written. Several meetings were attended as an observer to NBS-EPA negotiations regarding research for problems related to infiltration of radon in the environment.

STRUCTURAL METHODS FOR PROCESSING, MANUFACTURING, AND DURABILITY
Task 12153

The program of the Crystallography Group is applied both to this task and to Task 12155, Durability of Ceramics and Glass in Service Environments. The latter portion of the program is reported in Task 12155. The objectives of the program are to: provide x-ray and thermal expansion SRM materials; compile and disseminate Crystal Data; prepare and publish standard x-ray patterns with JCPDS--International Centre for Diffraction Data; develop a new high pressure x-ray method for radial distribution of liquids and amorphous materials, correlate with and extend range of our viscosity measurements; determine the PT behavior of semiconductors by optical, x-ray and/or electrical measurements; determine structures of compounds of interest to industry and government (FDA); develop measurement methods for selected area diffraction and compound analysis; and improve measurement methods by x-ray diffraction of spacings and intensities using automation and computer analysis.

New programs initiated this past year include the characterization of fly ash from various fuels and power plants for the Office of Recycled Materials and DOE, nuclear solid wastes for DOE, determination of the partial structure factor of glassy metals as a function of pressure for DOD and, in cooperation with NRL, the design and construction of a crystallographic line for the synchrotron source at Brookhaven. The relationship with the JCPDS--International Centre for Diffraction Data has been strengthened by hiring a senior scientist for the associateship. Information for ongoing and new programs such as the preparation, characterization, and certification of silicon dioxide polymorph SRM for NIOSH is presented below.

Crystal Structure Analysis and Materials Characterization
Subtask 1 of Task 12153

A. D. Mighell, C. R. Hubbard, J. K. Stalick, V. L. Himes

The combination of single crystal and powder diffraction methods with the Crystal Data and Powder Data Files and with recent developments in lattice theory (collaboration with A. Santoro) represents a unique capability for structure work and materials characterization. Consequently, many collaborative projects with other groups at NBS and with university and industrial scientists have taken place during the year. One student, R. M. Doherty, who has carried out three structure determinations with us, will receive her Ph.D. from the University of Maryland in August 1980; a second student, M. J. Lynch, who has completed one structure with us will complete his thesis (University of Maryland) in the fall; and a third student, V. L. Himes, an NBS-Catholic University COOP student, who has completed structures and theoretical work with us, is well along toward completion of her work toward her Ph.D. degree. Several structures in collaboration with the FDA (S. M. Page and W. H. DeCamp, guest workers from FDA) have been carried out and a structure with Allen Siedle of the 3M Company has been determined.

To improve our facility we are: (a) adding an up-graded module to the Syntex diffractometer which will allow more control over data collection, (b) linking the Crystal Data File to the Syntex diffractometer for characterization, and (c) implementing improved methods to characterize lattices. Specifically, J. K. Stalick has devised an elegant procedure that will allow one to interactively reduce cells and calculate powder patterns for a rapid characterization and evaluation of materials; V. L. Himes has worked out and applied a method for symmetry determination that has a number of advantages over existing procedures (see below); and C. R. Hubbard and J. K. Stalick have greatly augmented the AIDS program which is especially useful in materials characterization.

During the year, a number of structures have been solved and materials characterized. Below we give examples of structure work carried out: (a) the structure of a corrosion inhibitor, (b) the structure of an electron-donor-acceptor complex, and (c) typical FDA structures. Also we give a brief summary of work carried out on lattice theory and the application of lattice theory to materials characterization.

Lattice Theory: (Collaborative work with A. Santoro) During the year considerable work has been carried out in the areas of lattice/formula registration and symmetry determination. This work has many applications with respect to materials characterization and to the understanding of materials properties that are lattice dependent.

Registration: Data files containing diffraction information on solid state materials are rapidly expanding. Consequently, it has become necessary to develop computer techniques to register materials entering large data bases of solid state materials. Registration based on lattice parameters and empirical formulae is especially effective. In our present registration procedure, the lattice is uniquely represented by the reduced cell and the elements in the formula are uniquely specified by prime numbers. Such a method has been applied for several years to register new materials entering the Cambridge Crystallographic Data File and is currently being adapted to register materials entering the NBS Crystal Data File. The Cambridge File contains data on over 25,000 carbon containing compounds. For these materials, we have found that lattice/formula registration is extremely effective. In fact, our experience shows that it would be highly desirable if organic materials were routinely characterized by cell parameters in addition to traditional chemical analyses. A solid-state registry number which would allow one to identify the same compound in different data bases could also be based on lattice/formula and allow one to distinguish polymorphs.

Registration procedures will be greatly expanded by matrix techniques (Santoro, Mighell, and Rodgers, Acta Cryst., in press) which will allow one to establish many types of lattice relationships. For example, by using these techniques, derivative lattice relationships can be immediately established. The registration program, with minor modifications, can be converted into an identification program that can be used in conjunction with the Crystal Data File for materials characterization and identification. A general program is being written in RATFOR (rational FORTRAN) by John Rodgers (of the Unversity of Adelaide) that is designed to be transportable (i.e., machine independent).

Symmetry: In a paper published this year (Acta Cryst. A36, 321) it was shown, based on an analysis of the data in the Crystal Data File, that there is a close correlation of metric (size and shape of the unit cell) with crystal symmetry. Clearly, in the experimental determination of crystal symmetry, one should first determine the metric symmetry. For example, one can quickly prove that a crystal is triclinic from the metric symmetry alone. In the analysis of the cells with our crystal data evaluation program (AIDS), symmetry is determined via reduction techniques. Although reduction procedures are perhaps the most reliable for symmetry determination, there are several non-trivial problems with this method when used automatically without any human interaction. First, experimental errors cause problems in treating the inequalities inherent in the special conditions for reduction. In some cases, it is difficult to establish a single "correct" reduced cell for the lattice. Second, in using reduction procedures, one must transform an experimentally determined cell to the reduced cell. Third, it is difficult to establish pseudo-symmetries. Consequently an alternative method to determine symmetry is being developed.

In a recent paper (Santoro, Mighell, and Rodgers, Acta Cryst., in press), it has been shown that the lattice relationships can best be understood by determining matrices that relate cells in the same or different lattices. An algorithm ($\underset{\sim}{B}$-matrix) to determine such matrices was presented. As part of her thesis work, V. L. Himes has developed a routine analytical technique (based on a modified B-matrix algorithm) to determine lattice symmetry. In using this technique, one finds all the transformation matrices with integral coefficients (range 0-20) that relate the cell to itself. One then determines the symmetry from the set of matrices obtained. The method is superior to reduction in a number of ways. With this technique, one can simply determine the lattice symmetry from whatever cell has been determined without transformation of the cell to a standard or reduced cell. The most important features of this method are that one can determine the highest possible metric symmetry within whatever tolerance one specifies, that pseudo-symmetries are immediately transparent, and that the method is inherently simpler and safer than reduction as one does not need to worry about the inequalities inherent in reduction theory. The technique has been successfully applied to a series of experimental problems in our laboratory.

Corrosion inhibitor for copper: (V. L. Himes, thesis work) Benzotriazole (BTA) is a widely used corrosion inhibitor for copper. To help elucidate the nature of the protective film formed by benzotriazole on copper, we have solved the structure of a coordination complex between the anion BTA^- and copper. The structure solution revealed a new and novel bonding mode for BTA in which three contiguous nitrogen atoms in the same ligand are coordinated to three different copper atoms.

The complex ($C_{56}H_{60}Cu_5N_{22}$) crystallizes in the tetragonal crystal system, space group $P\bar{4}2_1c$, unit cell parameters a = 13.836(4) A and c = 16.686(4) A, Z = 2, d_{obs} = 1.41 and d_{calc} = 1.413 g cm^{-3}. There are two neutral complex molecules in the unit cell, one at the origin and one at the center of the cell. A view of the complex down the c-axis is shown in figure 1 (for clarity only three nitrogen atoms of the two benzotriazole ligands coordinated along the c-axis are shown and the entire molecule at the orgin has been omitted). The large neutral complex has 4 symmetry with a central Cu+2 atom in octahedral coordination to six BTA^- ligands. These same ligands bridge the central Cu+2 ion to four Cu+1 ions each of which is tetrahedrally coordinated to three BTA^- ligands and one t-butyl isocyanide ligand.

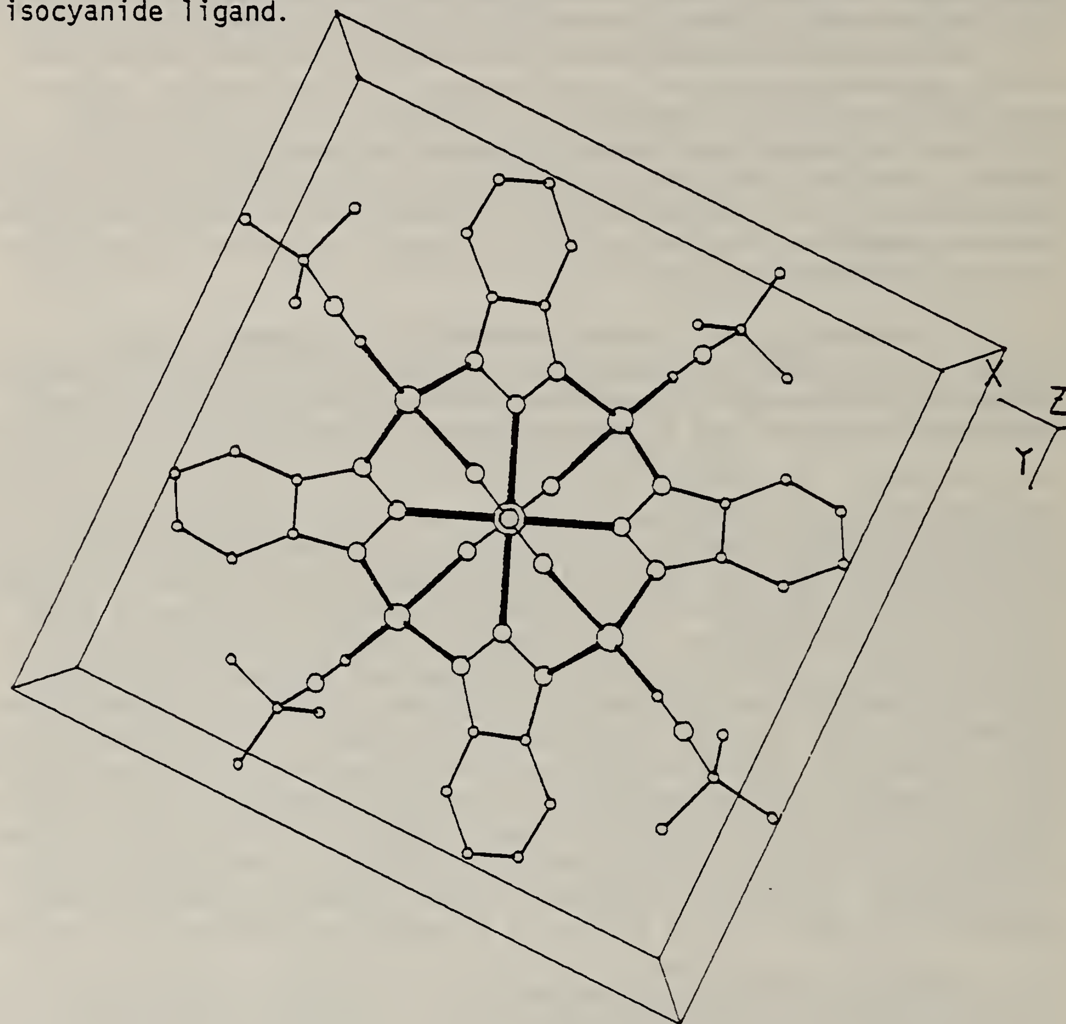


Figure 1. Copper Benzotriazole Complex ($C_{56}H_{60}Cu_5N_{22}$)

Electron-donor-acceptor (EDA complex) (R. M. Doherty thesis work) A molecular complex between two molecules may be defined as an association of definite stoichiometry that is stronger than a van der Waals attraction. Complexes involving pyrene fall into the class of molecular complexes known as electron-donor-acceptor (EDA) complexes. Such complexes involve an association between a donor molecule of low-ionziation potential and an acceptor molecule of high electron affinity. In the compound in this study, the donor is pyrene and the acceptor is a substituted cyclopentenedione.

The crystal structure analysis was carried out to determine the molecular parameters of this complex. The complex crystallizes in the triclinic space group P1 with·two donor and two acceptor molecules in the unit cell. The two acceptor molecules are centrosymmetrically related to one another. However, each pyrene lies on a center of symmetry, so that the two pyrenes are crystallographically independent of one another. The packing consists of stacks of alternating donor and acceptor molecules (figure 2a) along the body diagonal of the reduced cell (in a similar potential charge transfer complex) (V. L. Himes, thesis work), the stacks were found to be along the shortest unit cell dimensions (figure 2b). The least-squares planes of the molecules are not quite parallel to one another. Such non-parallelism of the molecules in other EDA complexes has been cited as evidence of specific localized interactions, presumably of the charge transfer type, between donor and acceptor.

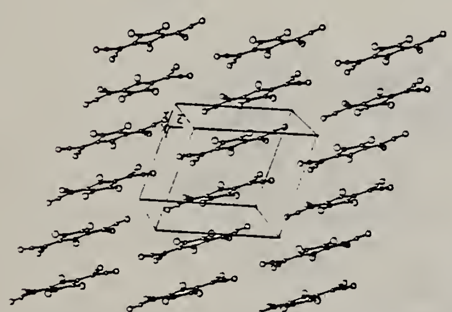


Figure 2a

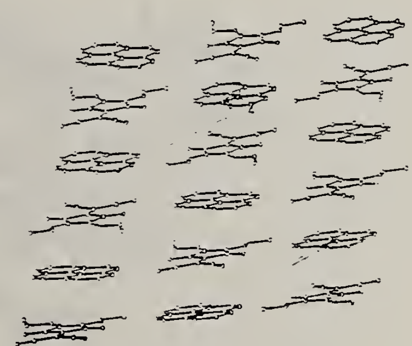


Figure 2b

FDA Structure Work: The FDA structure program has been stabilized with respect to funding and materials to be studied. Samples are being prepared by several groups at FDA. In this work special emphasis is placed on: (a) the correlation of drug stereochemistry with its biological activity, (b) polymorphism in drugs, and (c) molecular structure of toxins.

From stereochemical data, one can establish the basis for rationally designed drugs for the treatment of such diseases as cancer. This year a paper was published on 4-phenylcyclophosphamide, a compound that is closely related to cyclophosphamide (CP) which is a well known drug for the treatment of a broad spectrum of human cancers. (figure 3)

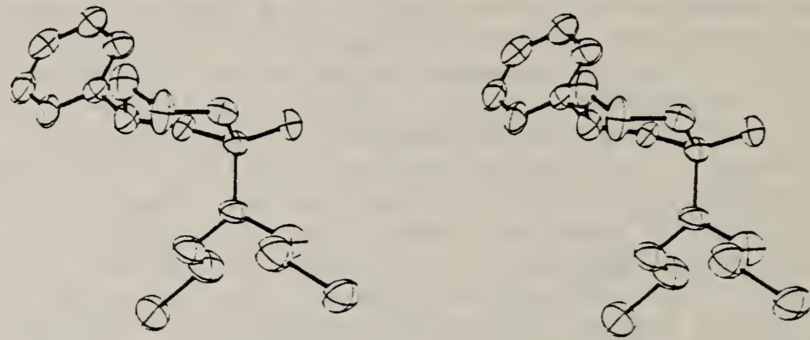


Figure 3. 4-phenylcyclophosphamide

From data on polymorphism, one can establish correct dosages of drugs. It is essential that drug preparation and crystallization procedures be carefully monitored to assure that one obtains the desired polymorphic form. During the year we have solved the structure of one polymorph of Carbamazepine, an important commercial drug, and we are starting to work on a second form. We plan to relate the two forms and to study the conditions under which they form.

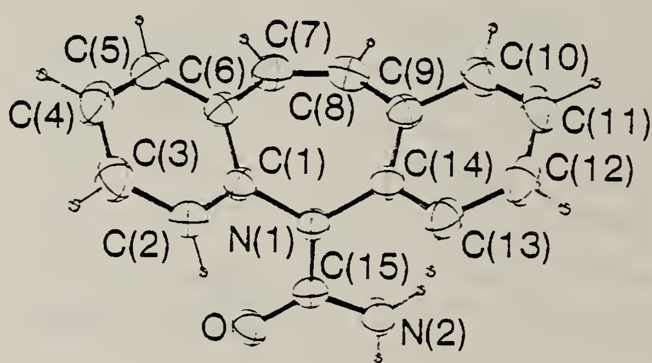


Figure 4. Carbamazepine

From data on molecular shape, one can attempt to understand the mechanism of a toxin. The structure of xanthomegnin ($C_{30}H_{22}O_{12}$), a toxic metabolite of a pathogenic fungi, was solved and found to be significantly different from what the chemist thought. The molecule crystallizes in a tetragonal space group and is shown in figure 5.

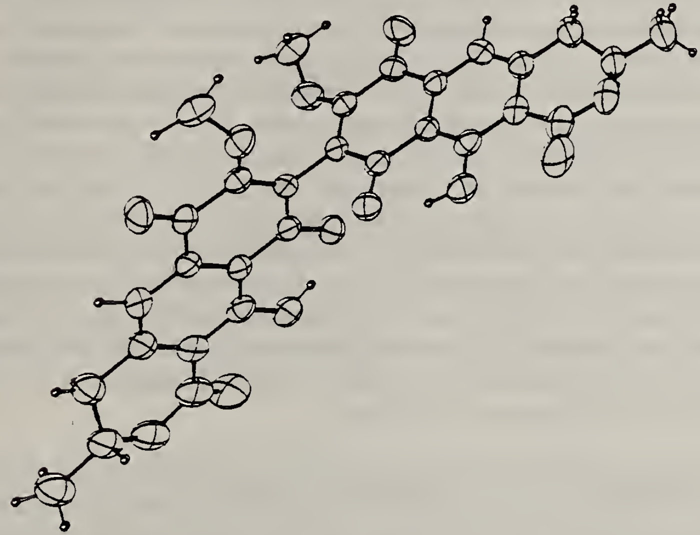


Figure 5. Xanthomegnin

Crystal Data
Subtask 2 of Task 12153

A. D. Mighell, J. K. Stalick, R. J. Boreni

The recent emphasis of the Crystal Data project has been on the conversion and expansion of all phases of the data operation (input, evaluation, and dissemination) to computer-based procedures. A major effort has been made to establish the best format for a master data file that will serve the internal operations of the project as well as the needs of the scientific community. This effort has been aided by the completion of the analysis of a questionnaire sent to users of Crystal Data products. To date over 3500 volumes of Crystal Data have been sold.

Automation of NBS Data Centers: A principal objective of the Office of Standard Reference Data (OSRD) is to increase the automation of the various data center operations. The increasing size of the data bases requires computerization for efficient editing, evaluation, and dissemination of the data. The Crystal Data project was selected as a prototype for complete conversion to a computer-based operation, particularly with respect to the creation of a master data file that can be used for on-line searches, product generation, and research analyses. The project is to develop convenient methods to build a master data file and assist the durability data centers, as well as other OSRD data centers, in file design and manipulation. Cooperation in the design of file formats is essential; it permits compatible on-line dissemination of the various data bases, allows for a common assignment of chemical registry numbers, permits the writing of efficient typesetting software, and greatly simplifies software problems in that common editing and data base management routines can be used.

Construction of the Master Data File: The input procedures, content, and format of the master data file have been completed during the year in collaboration with C. R. Hubbard of NBS and with the Cambridge Crystallographic Data Centre, the Joint Committee on Powder Diffraction Studies (JCPDS)--International Centre for Diffraction Data, and the Metals Data Center (Ottawa). The NBS Crystal Data File and the JCPDS Powder Diffraction File have been designed with a common format to permit common input and data manipulation procedures, joint data evaluation routines, and common data dissemination and publication techniques. Moreover, common evaluation of single crystal data and powder data enhances the quality of both data bases.

(1) Format: The content and format specifications for the master data file have been completed, and preliminary documentation has been written.

(2) Data Input: Computer programs have been written to allow for data input via computer terminals. A computer "form" is used to input data base entries and record them on magnetic tape cartridges, and a preprocessor program (C. R. Hubbard) has been

written to convert the data to the proper format. A program has also been written for interactive on-line data input for research analysis runs.

(3) Evaluation and Data Base Building: The computer programs AIDS has been extensively rewritten in collaboration with C. R. Hubbard. The program evaluates the data, checks for consistency, transforms the data to standard settings, and builds a data base entry. Evaluation routines include transformation of the original unit cell to the Crystal Data cell and the reduced cell, assignment of a quality index to cell parameters, transformation of space group and assignment of space group number, and flagging of unusual values. The chemical formula is analyzed for legal element symbols, and an empirical formula, molecular weight, and density are calculated; the calculated density is then compared with the authors' measured and calculated densities. Journal references are checked for legal CODEN's, and journal abbreviations are printed. The reduced form and reduced form number are determined, and the metric symmetry is compared with the reported crystal symmetry. Powder pattern analysis includes calculation of d-spacings, indexing of lines, comparison of observed and calculated powder lines, and calculation of figures of merit.

Data Registration and Identification Procedures: Registration procedures are used to find out if the same entry, or a related entry, is already in the data base so that evaluation can be carried out with respect to the set of known data. The registration software based on the crystal lattice and chemical formula is being written in collaboration with J. M. Rodgers, University of Adelaide, and the procedure will be published.

Crystal Data Identification File: A high priority has been set on the preparation of a distribution file with four lines per entry for the rapid identification and characterization of unknown materials. The file is being prepared in collaboration with the Cambridge data center and OSRD with a target completion date of late 1980. It contains the reduced cell, space group and space group number, cell volume, density, chemical name and formula, literature reference, and reference to Crystal Data Determinative Tables for approximately 60,000 substances. The Chemical Abstracts registry number will also be appended to the file. The names and formulas of inorganic substances have been extensively revised so that the nomenclature follows consistent rules, thus permitting computer searching and typesetting. A simplified version of the file has been used during the year to identify substances for the FDA and the JCPDS, and the procedure has been quite successful.

The initial mode of file dissemination will be on-line through the Chemical Information System (CIS). The CIS interactive search software is now working on a limited test version of the file. Other potential modes of dissemination are being explored. The identification file can be distributed to national data centers for use within the country; one such center in Germany has already requested lease of the file, and it is likely that other data centers affiliated with the Cambridge data center will also be interested in leasing the file. One manufacturer of automated diffractometers is considering incorporating the file, with appropriate search software, into their instrument so that a cell can be determined and the substance identified automatically. The file could also be made available on tape for private use, and publication of a printed version is also under consideration.

The use of the file for identification of substances was presented at a special session on crystallographic data bases at the American Chemical Society meeting in Washington, D.C., in the fall of 1979. Other types of research applications are possible. For example, a systematic density analysis was carried out on similar data in the Cambridge file by a scientist at Lawrence Livermore Laboratory. Also, we have found through analysis of the file that the crystal symmetry can almost always be deduced from the unit cell parameters alone; a paper on this subject entitled "Lattice Symmetry Determination" was well received, and should lead to rapid and more accurate symmetry determinations on a routine basis.

<u>Research Applications of AIDS</u>: The evaluation routines in the computer program AIDS should also be of value to the general scientific community. Evaluation of data prior to publication will lead to better data in the literature. We are preparing a version of AIDS for public release. The programming is near completion, and a preliminary documentation has been prepared. Standard ASCII FORTRAN has been used to permit use on a wide variety of computers, and the program has been modified to accept input from computer terminals or punched cards. The availability of the program and its research applications was presented in August of 1980 at the American Crystallographic Association meeting in Calgary and at the Denver X-ray Conference.

<u>Computer Manipulation of Data</u>: During the year considerable computer time has been made available from the Director to the Crystal Data project. This has allowed us to change our mode of operation from a batch to an on-line mode, and the on-line editing has proved to be much more practical and efficient than batch methods. The additional computer time, moreover, has allowed us to develop and to test procedures for the management of large data files. The handling of large files on the UNIVAC has proved to be much easier than expected and clearly demonstrates that a large computer with adequate software is to be preferred for large data files.

<u>Analysis of Questionnaire Response</u>: The analysis of the response to the questionnaire on <u>Crystal Data</u> was completed and published as NBS Technical Note 1112. The results indicate a high frequency of use of <u>Crystal Data</u>, with particular application to materials analysis and design. The survey suggests a need for the development of a rapid and inexpensive method of unit-cell determination as well as education of the scientific community in the use of the single-crystal method for identification of unknown materials. More complete coverage and con-

solidation of entries are also suggested. The necessity for computer-based methods of data base dissemination is indicated, with particular importance for research applications.

Powder Diffraction
Subtask 3 of Task 12153

C. R. Hubbard, S. J. Carmel

Automation: Two powder diffractometers are now operating under control of the Interdata 7/16 minicomputer. The control program AUTO, written by R. L. Snyder (Alfred University), C. R. Hubbard and N. C. Panagiotopoulos (JCPDS), is an interrupt-driven executive which permits execution of various sub-algorithms (pattern collection, data collections, quantitative analysis, file transfers, counting, stepping, termination, etc). For quantitative analysis the time spent counting the background and peak regions can be optimized within the constraint of a preselected total time or preselected statistical error. The actual data collection parameters are prestored on a run file produced either on the mini or the Univac 1108. The output data file contains a complete definition of the instrument, the run paramaters, and the experimental data. Because of limitations of memory and operating system all data will be transferred to the Univac 1108 for analysis. Currently this is achieved by means of floppy disks. In the near future it should be possible to access the NBS net and transfer any ASCII file between the mini and the U1108 at 9600 baud.

Computer Analysis of Powder Patterns: A digitally recorded powder pattern is processed on the Univac 1108 using a set of programs developed at Alfred University by Dr. C. Mallory and Professor R. L. Snyder. These programs use second derivative peak finding algorithms and allow α_2 stripping, data smoothing, and background subtraction. A coordinated set of graphic programs has also been implemented to produce plots on a Tektronics 4012 terminal (purchased by the JCPDS) for examination by the experimentor. This capability has been found to be essential as it maintains input from the diffractionist in the interpretation of the digital data. Analysis of overlapping profiles will be added to the analysis capability early in FY81. Profile analysis will significantly improve the quality of d-spacing and intensity measurements of overlapping lines. Extensive enhancement of the plotting capability is also planned. This includes the potential to direct the plots to other plotting devices and to permit user interaction at the Tektronix terminal. A program for 2θ calibration using an internal standard, such as SRM 640 Si powder, has been written. The program allows for precorrection for known systematic errors and then fits a polynomial through the correction based on the internal standard lines. The lines of the unknown are then corrected and the corrected 2θ's and $\sigma(2\theta)$'s are output. The program will be expanded to allow for external calibration and for choosing the order of the polynomial based on a goodness-of-fit criteria.

Quantitative Analysis: A program POWDER*QUANT which can be used for three methods of quantitative analysis by x-ray powder diffraction has been written by Professor R. L. Snyder (Alfred University) and

C. R. Hubbard. The program allows for analysis by the internal standard method (see SRM's below), the known chemical composition method and the spiking method. The automation system discussed above is programmed to intelligently collect the appropriate data for each method.

The algorithm allows for overlapping lines as well as imposition of flexible external constraints such as $\Sigma x_i = 1$ and/or chemical analysis. The program uses the L. E. Copeland and R. H. Bragg procedure for overlapping lines as generalized by C. R. Hubbard to incorporate the Reference Intensity Ratio (I/Ic) and relative intensities. The program POWDER*QUANT can also be used to determine relative intensities and the Reference Intensity Ratio. X-ray powder diffraction analysis is being extended in an attempt to analyze for the percent amorphous phase in a sample. The procedure involves integrating the area under the amorphous hump in the diffraction intensity. Both the internal standard and the spiking analysis methods will be tested to determine sensitivity. If successful this technique will be used in analysis of glass content in fly ash samples and the percent crystallinity in quartz, cristobalite and tridymite candidate SRM samples.

Standard Reference Materials: The certification of α-Al_2O_3, TiO_2 Rutile, ZnO, Cr_2O_3, and CeO_2 for powder diffraction intensity standards has been completed. The cell parameters, the relative intensities, and the Reference Intensity Ratios (RIR) are given in order that the materials may be used as an internal standard in quantitative analysis by x-ray powder diffraction. Procedures and pitfalls of calculating and measuring the Reference Intensity Ratio were previously reported. This information coupled with these SRM's simplify the task of performing a quantitative analysis. The resultant accuracy is limited by sample preparation (a serious problem) and the standards. The accuracy of the RIR and I^{rel} values are between ± 2 percent and ± 5 percent depending on the phase. The relative intensities for each phase were measured for samples prepared in a variety of methods including side drifting, spray drying, and coating with krylon. Both stationary and rotating samples were employed. The calculated and average relative intensities generally agree within ± 1 or ± 2 on the relative intensity scale (I_{max} = 100) except for α-Al_2O_3 where the differences have been ascribed to the use of a spherical approximation for the electron density about the atoms. The Reference Intensity Ratios were determined from measurements on all possible binary mixtures, each prepared at two or three different weight fraction ratios. The internal consistency and the agreement with calculated values was better than 5 percent.

Candidate materials for a large d-spacing SRM have been selected (wet ground muscovite mica and fluorophlogopite synthetic mica). Each of these materials exhibit 00ℓ preferred orientation when pressed which reduces interference with sample lines. Another candidate, thallous hydrogen phthalate, can be used to calibrate sample lines below 30° 2θ but not above 30° due to its increasingly complex pattern. Bulk samples will be ordered by September 30th and certification completed early in FY81.

Future SRM projects include certification of quartz, cristobalite, and tridymite powders for percent crystallinity, lattice parameters, relative intensities, and Reference Intensity Ratio. This project will be performed in collaboration with Dr. R. L. McKenzie (553-Gas and Particulate Science) with support from NIOSH and OSRM. The OSRM is also supporting development of a crystallite size standard in collaboration with Dr. A. L. Dragoo (561-Chemical Stability and Corrosion). The proposed phase is MgO which can be crystallized in the 100 to 2000 range by precipitation-decomposition methods as well as by condensing a smoke onto a cold surface. The latter method may yield individual crystallites whose dimensions can be measured by electron microscopy. Such measurements will be valuable as a primary reference method for checking and/or calibrating the Fourier line broadening analysis.

Standard Patterns: Six associates of the JCPDS--International Centre for Diffraction Data (M. C. Morris, Director; H. F. McMurdie, Consultant; E. H. Evans, B. Paretzkin; N. Panagiotopoulos; and C. Wingo) along with S. J. Carmel and C. R. Hubbard continue to produce high quality x-ray diffraction patterns as well as evaluate and edit data from the literature. Section 17 of NBS Monograph 25 will be published in September 1980. This is the 26th of the series of "Standard X-ray Diffraction Patterns". Section 17 will include approximately 60 experimental patterns as well as a review of methods used at NBS for obtaining the patterns.

Each year the JCPDS publishes a supplement to the powder data file (PDF). The complete file, recognized as the standard reference source for powder diffraction analysis, consists of 29 sets of data for nearly 33,000 crystalline phases. Due to the continuous growth of the PDF, a major effort of the JCPDS is to produce subfiles for selected fields. Subfiles currently available are: (1) Frequently Encountered Phases (FEP)/Common Phases (CP), (2) Minerals, (3) Metals and Alloys, and (4) NBS Patterns. M. C. Morris, Chairperson of the FEP/CP subcommittee continues to review and improve that subfile. Under her direction the Associateship is adding to the PDF new patterns and replacing poor patterns with high quality data. Approximately 90 percent of the patterns, both organic and inorganic, to be published in Section 17 of the Monograph have been designated for the FEP/CP subfile. For FY81 the group expects to submit approximately the same percentage. The remaining ten percent of the patterns are of less common phases of minerals, alloys, forensic, or ceramic materials for which samples were available and the pattern was absent or not well represented in the file.

The Associateship continues to work on methods and procedures that are useful to the diffraction community. For instance, a considerable amount of time is being spent on finding means of obtaining reliable intensities. During FY80, the group began reporting a reproducibility factor for the measurement of relative intensities. This factor enables a user of the data to evaluate the accuracy of the intensity data. Also, in accordance with the recommendation from the American Crystallographic Association, the Associateship now includes in its publication of data a figure of merit (FM). This FM enables one to assess the quality of the experimental spacing measurements.

JCPDS Activities: NBS staff members (S. Block, C. R. Hubbard, and A. D. Mighell) continue to participate in activities of the JCPDS. Of particular importance has been a thorough review of the JCPDS-NBS Research Associateship. Following this review, the RA has shifted its emphasis to producing more high quality experimental patterns and fewer calculated patterns. To stay abreast with the developments in automation and digital pattern analysis, Dr. N. Panagiotopoulos was hired for the joint NBS-JCPDS diffractometer automation and data analysis project (discussed above). To assist in the preparation, purification, and crystallization of needed phases H. S. Parker will join the RA on a part-time basis in FY81. The two-year goal is to increase the output and data quality of the RA.

The Education Subcommittee (C. R. Hubbard, Chairman) has completed a major revision of the PDF Workbook which is used at tutorials on use of the Powder Diffraction File. This tutorial course has been presented to about 200 diffractionists at the Denver X-Ray Conference, SUNYA X-ray Clinic, and Pennsylvania State University. The Workbook is coordinated with the JCPDS-NBS book of high quality reference patterns.

The JCPDS Data Base Task Group (including C. R. Hubbard, Chairman, and A. D. Mighell of NBS) has recommended to the JCPDS that they adopt the program NBS*AIDS80 and the HP2645 CRT formatting terminal for data entry. Both NBS*AIDS80 and the input forms for the terminal (with some assistance from the JCPDS) have been developed at NBS as a common data input and evaluation system for Crystal Data and the JCPDS. The proposal was approved and implementation is beginning. The Metals Data Center (NRCC-Canada) and the Cambridge Data Centre are considering adoption of part or all of this system. The program is also being made available to researchers and journal editors in an attempt to improve the quality of powder diffraction patterns and unit cell data in the primary literature. Such a program was envisioned by a subcommittee of the American Crystallographic Association, which drafted guidelines for publication of powder patterns.* C. R. Hubbard was one of the members of this subcommittee.

A critical part of the JCPDS's conversion to use of NBS*AIDS80 is to merge and reformat their ∿ 33,000 data base entries into the new data base structure. To begin on this task the various computer readable tapes containing portions of PDF data have been converted to a common format, merged, and then transformed into NBS*AIDS80 input format. We are beginning to process these through AIDS80, creating data base entries for each PDF card. This task has been performed by E. G. Speert a summer employee of the JCPDS under the supervision of C. R. Hubbard.

Other activities include the CIS task group (A. D. Mighell and C. R. Hubbard), Methods and Practices Subcommittee (C. R. Hubbard), Crystal Data Subcommittee (A. D. Mighell), and the Board of Directors (C. R. Hubbard).

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*The subcommittee's final report was presented at the IUCr-NRCC-NBS meeting Accuracy in Powder Diffraction (June 1979).

Diffraction Instrumentation
Subtask 4 of Task 12153

F. A. Mauer

Equipment: During the past year, two instruments have been installed that provide NBS with new capability for obtaining powder diffraction data from very small amounts of material, or from a selected area of larger samples. The Gandolfi camera, which is suitable for examining isolated particles consisting of a few crystals with a total volume of the order of 10^{-3} mm^3, will be used in characterizing particulates from environmental samples related to fossil fuel technology.

The Rigaku microdiffractometer, on the other hand, is used when the material to be examined cannot be separated from its matrix. Inclusions in an MHD electrode or material recovered from the diamond anvil pressure cell (which cannot be separated from the gasket) would be typical of the samples examined with this instrument. These instruments supplement the existing x-ray diffraction and SEM capabilities for analysis by furnishing information about compound formation in minor phases or inclusions.

Synchrotron Radiation Facilities: Scientists from NBS and from the Naval Research Laboratory have formed a "Participating Research Team (PRT)" for the purpose of carrying out the design and instrumentation of two beam lines at the National Synchrotron Light Source under construction at Brookhaven National Laboratory. The facility, which is scheduled to begin operation late in 1981, will provide an intense source (10^4-10^6 higher than conventional sources) of highly collimated, polarized x-rays in the approximate range from 6 to 25 keV (2 to 0.5A). Use of monochromators to select appropriate wavelengths from this continuum will enable the experimenter to utilize anomalous dispersion effects for specific elements in order to obtain phasing information in single crystal structure determinations or pair correlation functions in the case of glassy materials including thin films. The intensity of the source can also be used to reduce the time required for certain experiments that would not be feasible with conventional sources. NBS is cooperating with scientists at the Naval Research Laboratory in designing a monochomator system and a general purpose goniometer that will be suitable for a number of different types of experiments. Special detection equipment will also be required to handle the extremely high peak counting rates encountered in research with a synchrotron source. A decision has not yet been made about developing a position sensitive detector system on the one hand, versus a single channel detector on the other. Meanwhile, experiments are being planned that will exploit the unique tuneable wavelength, high intensity features characteristic of synchrotron radiation.

A rotating anode x-ray generator, purchased in cooperation with Division 564, has recently been installed at NBS. It has an x-ray output ten to fifteen times greater than that of conventional x-ray generators and will be very useful in testing and aligning experimental apparatus for later use at the synchrotron. It will enable us to obtain data with the diamond cell at ten times the present rate or at substantially higher resolution.

Powder Materials Characterization and Analysis
Subtask 5 of Task 12153

C. R. Robbins

Refractories for Coal Gasifiers: Work with the Fracture and Deformation Division (S. M. Wiederhorn, E. R. Fuller, Jr.) in the form of phase analysis of candidate refractories and cements for coal gasification reactor linings has been completed. Analysis was by conventional x-ray methods on materials previously exposed to simulated gasification environments. A final report has been prepared for the Department of Energy. (See Task 12155)

Structural Ceramics: At the conclusion of the refractories study, work was initiated on Si_3N_4, SiC, and sialons by F. A. Mauer and C. R. Robbins. This work is now in progress. It is a continuation of the collaborative effort with the Fracture and Deformation Division (E. R. Fuller, Jr., R. J. Fields), and is sponsored in part by the Department of Energy. (See Task 12155). The goal is to improve the operation of gas turbine blades and heat exchangers fabricated from these silicon compounds.

Characterization of Prehistoric Ceramics: A collaborative study with the Smithsonian Institution (V. P. Steponaitis, Predoctoral Fellow in Anthropology) of prehistoric pottery from Moundville, Alabama, has been completed. Moundville is the second largest Mississippian site in eastern North America and was occupied between A.D. 900 and A.D. 1600 by Indian tribes. Quantitative phase analysis by optical and x-ray methods has identified the raw materials used, and the range of firing temperatures reached in making the pottery. A detailed report on the mineralogy of the materials is planned.

Characterization of Power Plant Ash: This is a highly variable material. Its chemical composition and physical properties are primarily functions of fuel feedstock, variances in plant equipment, burning methods, station loading, aging, and collection, separation, and storage methods. Whether the ash is to be regarded and managed as a large volume mineral resource or as a hazardous waste remains to be seen. There is an urgent need for chemical and physical characterization of these materials.

A program to study power plant ash, sponsored by the NBS Office of Recycled Materials, was initiated in 1979. The study will involve development of quantitative methods of phase analysis by x-ray powder diffractometry and will be complemented by several instrumental methods of chemical analysis. The work will produce a body of information on the behavior of a broad spectrum of fuel feedstocks, burned in a variety of plants under known operating conditions. This systems approach has not been explored before. The study will provide data needed for ash management techniques and for a better understanding of leaching mechanisms. It could lead to improvements in precipitator and scrubber designs, and to better utilization of coal by-products.

Emphasis and resources of this project have initially been directed toward the development of quantitative x-ray powder diffractometry methods. This has been possible because of a collaborative effort between Professor R. L. Snyder of Alfred University and Dr. C. R. Hubbard of the NBS Crystallography Group in modifying existing software in order to utilize new, automated NBS x-ray equipment. Ancillary equipment for x-ray sample preparation is being constructed in NBS shops. It is anticipated that the quantitative x-ray powder capability will be available in August 1980.

Several suites of carefully selected and documented samples have been received from interested groups for analysis. The samples span a broad spectrum of feedstock, and have been characterized by preliminary qualitative methods.

Fossil Fuel Technology Waste Sampling and Characterization Program, Physical and Chemical Characterization: In May 1980 a new program under the sponsorship of the Department of Energy, and the technical management of the Laramie Energy Technology Center was established at NBS. The program involves several groups at NBS and one of its objectives is to establish the behavior of fossil fuel wastes subjected to a variety of leaching procedures. The program will involve interaction with the Analytical Chemistry Division. The Ceramics, Glass, and Solid State Science Division is responsible for the physical and chemical characterization of the specimens, both before and after leaching. Receipt of the first samples for analysis is expected in August 1980.

Emerging Technologies: On the order of forty specimens of refuse derived fuels (RDF) have been received from the Chemical Thermodynamics Division for x-ray analysis. This is a cooperative effort intended to complement their calorimetric work on these alternate fuels, and to contribute to the formulation of ASTM test procedures for these new materials.

High Pressure Research
Subtask 6 of Task 12153

S. Block, G. J. Piermarini, R. G. Munro

Activity during the last year has concentrated on three areas of research: (1) development of a low temperature capability for the diamond anvil pressure cell; (2) the continued search for pressure transmitting media which will produce hydrostatic conditions at higher pressures; and (3) the continued study of the pressure-temperature phase behavior and electrical properties of several semiconductor materials, some of which have potentially useful applications as high temperature superconductors and others which are ideally suited as fixed points on the pressure scale.

Low Temperature Capabilities in the Diamond Cell: To extend the versatility and usefulness of the diamond anvil cell we have developed a new low temperature capability which permits optical and electrical measurements to be made involve pressures in the 200 kbar range down to below -160 °C without sacrificing any of its room temperature advantages. The cooling system is relatively simple and consists of a cooling element attached to the cell which is surrounded by a very simple insulating box. Liquid N_2 and or cooled gaseous N_2 is passed through the cooling element under controlled flow and temperature conditions. The temperature is monitored continuously and to facilitate the computation and recording of the data a microprocessor has been added to the system. The cell can be cooled very rapidly, as fast as 15°/min. At the desired temperature only a small flow rate is required to maintain the temperature to about ± 3 °C. Desired temperatures have been sustained for as many as four hours without difficulty while measurements were being made. This development represents a new and important addition to the capabilities of the diamond cell.

Search for Pressure Transmitting Media to Extend the hydrostatic limit: In our continued efforts to extend the hydrostatic limit to improve the quality of measurements at higher pressures, we are studying the hydrostatic properties of rare gas solids Xe and Kr by the ruby line broadening method. In recent months much interest has been shown in this prospect because the rare gases form very soft solids at room temperature and a few kilobars pressure. This property makes them attractive candidates as possible hydrostatic pressure transmitting media.

We have developed procedures which permit us to use our low-temperature system for loading rare gases in the diamond cell. The procedures have been refined to where loading condensed gases krypton and xenon in a diamond cell at low temperatures is now routine. Our study of Kr was interesting because a new hydrostatic limit of 158 kbar was established (room temperature). Xenon's behavior was quite different. Low-level nonhydrostatic effects were measured at all pressures in this material. But an interesting observation was that the magnitude of the effect seems to sharply decrease and then gradually build up again repeatedly with increasing pressure. This suggests that the material is undergoing relaxation of shear stress through plastic flow. The method offers interesting possibilities in determining the shear strength of the material. The phase diagram of Xe was studied visually between 150° and -150° and up to 130 kbar. No additional polymorphism appears to exist in this region of pressure and temperature other than the solid-liquid phase boundary. At room temperature the freezing pressure is about 8 kbar.

The low temperature system has also been used to measure the temperature dependence of the hydrostatic limit in 4:1 methanol:ethanol. The data show slight curvature as the glass transition pressure decreases from 104 kbar at 24 °C to 50 Kbar at -50 °C. This latter value is consistent with the temperature dependence of the glass transition in alcohols.

Semiconductors: The temperature dependence of the semiconductor-to-metal pressure transition in CdS was studied by our new low temperature system down to -150 °C by both optical and electrical resistance methods.

The transition pressure appears to be nearly temperature independent over this temperature range. The values obtained by electrical resistance measurements were consistently less by 5 or 6 kbar than the pressures obtained by the optical method.

Energy dispersive x-ray measurements were made on several samples of CdS. All ultimately transformed to an electrically conducting NaCl phase which, at least initially, was opaque. The transition pressure was found to be variable. The reasons for this effect are being investigated.

The transition pressures for the semiconductor-to-metal transformation in ZnS and GaP were determined visually in a krypton environment. The transition pressure for ZnS was found to be the same (150 kbar) as determined in 4:1 methanol:ethanol. However, the GaP transition pressure (235 kbar) is about 10 kbar higher than found in 4:1 methanol:ethanol. This effect possibly indicates that the GaP transition is lowered by the greater stress or pressure distribution in the alcohol mixture.

Boron was investigated as a possible fixed point standard in the 400 kbar range. However, the results with the same sample on different runs were variable--ranging from approximately 300 to 400 kbar. Similar results were found in another laboratory using a supported anvil press. A possible explanation is that the transition in boron is highly susceptible to different stress patterns. At the moment it is not a promising fixed point. Preliminary plans are being made under the auspices of the International Union of Crystallography, Commission on Crystallography, at controlled temperature and pressure to carry out another round-robin similar to that on ZnS. A candidate material is GaAs.

<u>Theory</u>
Subtask 7 of Task 12153

R. G. Munro

Two projects, which might be called reliability studies, are nearing completion. The projects concern the statistical reliability of the interpretation of experimental data. One of those problems is the reliability of binary and tertiary partial structure factors of amorphous systems which are determined by either of two x-ray anomalous dispersion techniques. The "direct" technique uses directly the change in the scattering of x-rays which occurs near an atomic absorption edge. The recently proposed "derivative" technique involves a frequency modulation of the incident x-ray beam, which is assumed to have a tunable source such as a synchrotron, and the slope of the atomic scattering factor.

Beginning from an ideal system of partial structure factors, a pseudo-random number generator is used to simulate experimental error. The response to this input error is then computed. A typical example for a binary system AB is shown in figure 6. The logarithmic axis gives an estimate of the relative parameter error (derived from a general error matrix) for each of the three partial structure factors. These estimates are shown as a function of the relative change in the

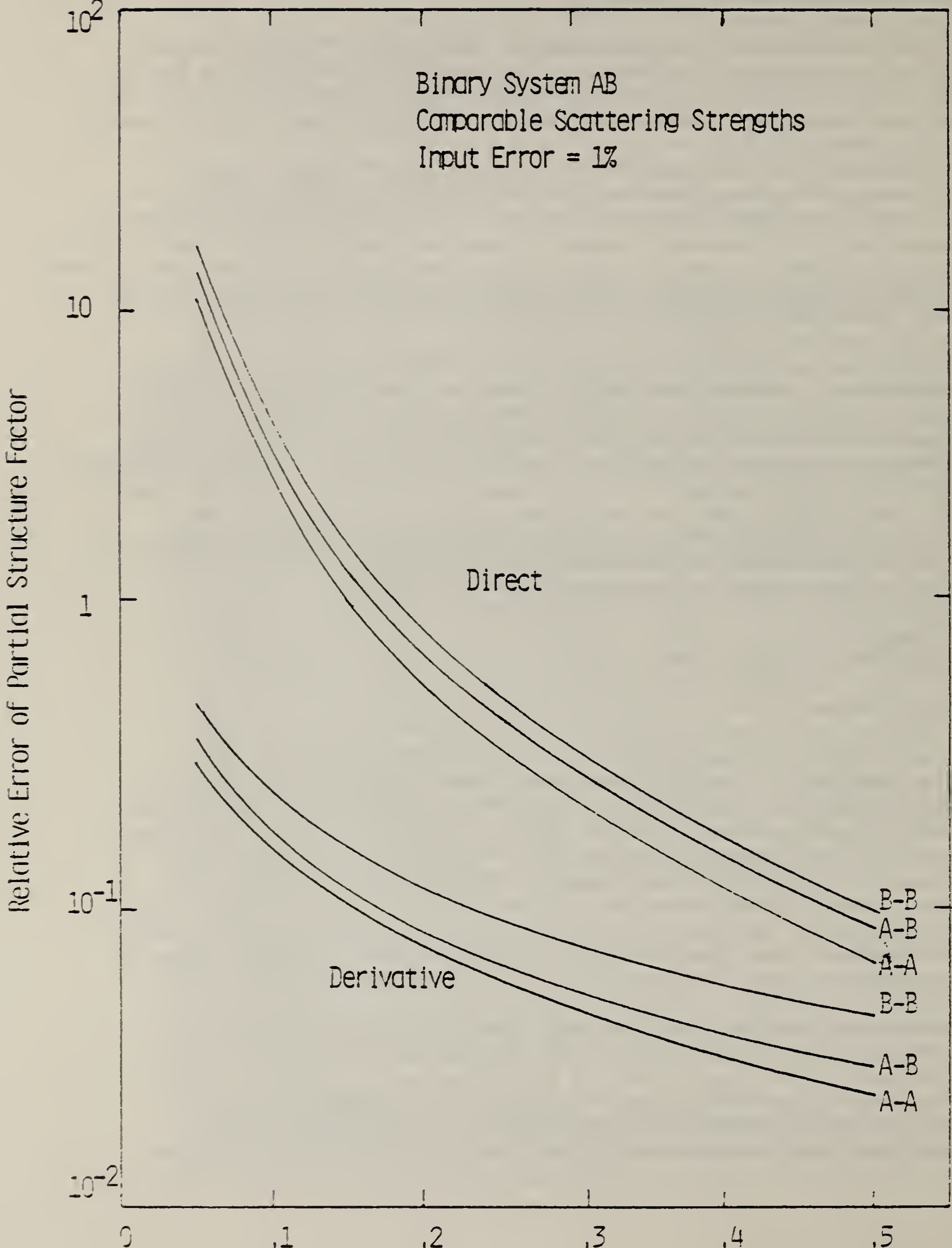


Figure 6. Relative Change of Atomic Scattering Factor

atomic scattering factors, x, under the anomalous dispersion conditions. The experimentally accessible range of x is about $0\underline{F}$ x $\underline{F}^{0}$ ^{3}. The case shown is for two comparably good scatterers and for a net experimental error of about 1 percent. Even under the best of conditions, the figure shows that the direct technique cannot be expected to yield an error lower than about 30 percent. Under the same conditions the derivative technique yields about 6 percent error which indicates that the experimental development of the derivative technique is highly desirable.

The second project growing from the viscosity-glass transition problem examines the very common problem of evaluating the parameters A_1 and A_2 in the simple model $y = \exp(A_1 + A_2 x)$ where x is an independent variable. The parameters are usually evaluated by means of a linearized least squared error method. However, it is not widely known that the fitting procedure that is used should be selected on the basis of the objective of the least squares fit and the type of error contained in the data. This work determines criteria for choosing the best least squares fitting technique.

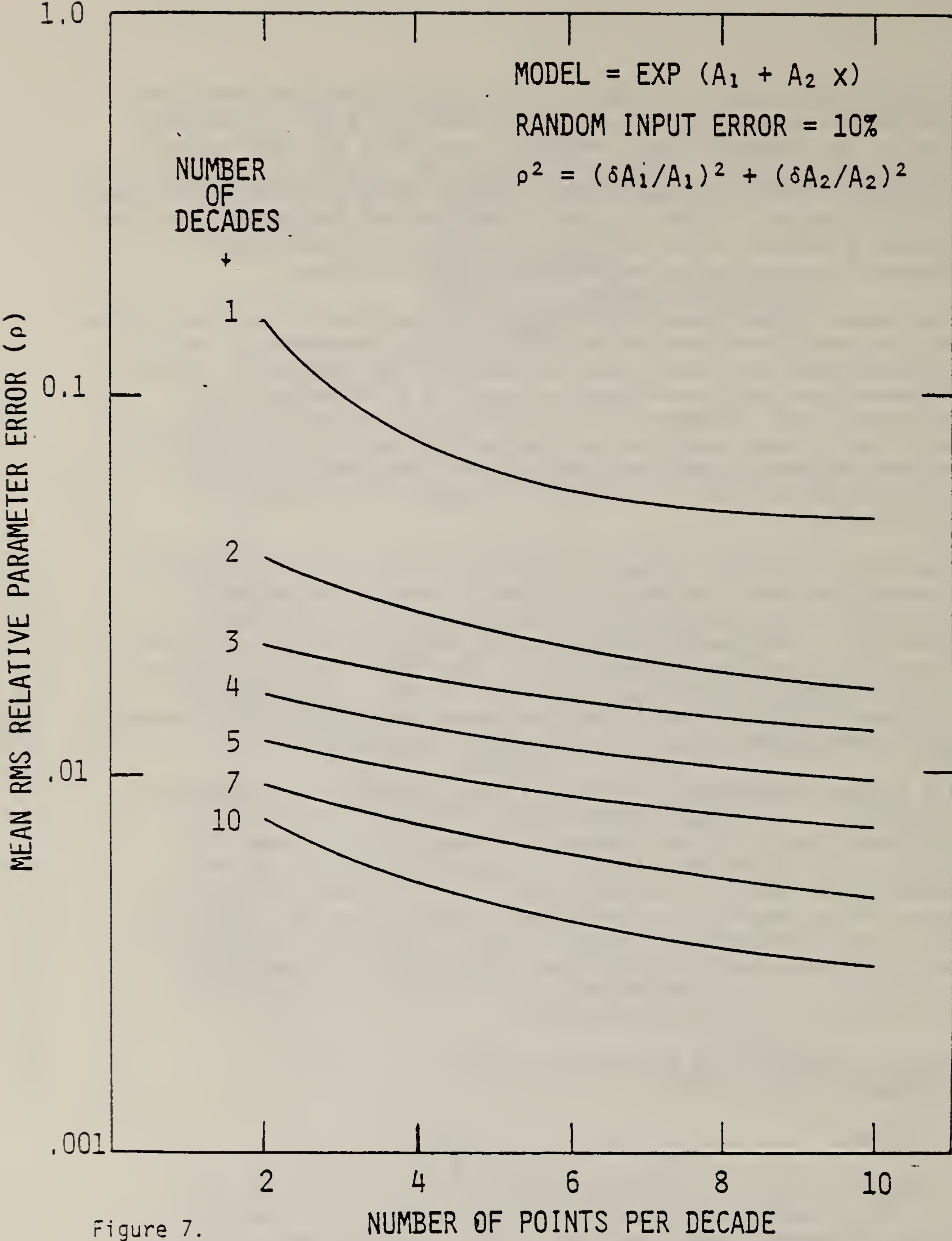
There are two distinguishable objectives: Obtain the best smooth curve through the data, and obtain the best values of the parameters. The latter case is the more complex of the two and does not have a unique solution. Consequently, criteria are obtained statistically and with these it is possible to determine the mean RMS relative parameter error as a function of the range and density of data. An example of this is given in figure 7 for a simulated experimental error of 10 percent. The numbers beside the curves give the number of decades of data.

The general conclusions that can be drawn from this investigation are as follows: (1) The best smooth curve through the given data is almost always given by the well known technique of using a modified weight factor. (2) The best values of A_1 and A_2 frequently do not correspond to the smallest standard error. (3) The range of data and the type of error determine a statistically best method for evaluating A_1 and A_2. (4) Increasing the range of data is generally more effective for improving the parameter values than is increasing the density of data. (5) The use of a modified weight factor does not significantly affect the value of the covariance matrix.

<u>Thermal Expansion and Nuclear Solid Waste</u>
Subtask 8 of Task 12153

T. A. Hahn

During this year, Mr. Hahn was assigned for six months to the Office of Measurements for Nuclear Technology as technical coordinator of a study group developing a program for DOE. The program, which is described in the group's report "Measurements and Standards for Nuclear Waste Management," will be funded in 1980 and will become an important activity of the Center for Materials Science.



MODEL = EXP (A1 + A2 X)
RANDOM INPUT ERROR = 10%
$\rho^2 = (\delta A_1/A_1)^2 + (\delta A_2/A_2)^2$
NUMBER OF DECADES
1
2
3
4
5
7
10
1.0
0.1
.01
.001
MEAN RMS RELATIVE PARAMETER ERROR (ρ)
2
4
6
8
10
NUMBER OF POINTS PER DECADE

Figure 7.

Despite manpower limitations, measurements are being completed on a new stock of copper for SRM 736. The original material was sold out a few years sooner than had been anticipated showing the good sales of these important SRM materials.

Initial plans were developed for hosting the International Thermal Expansion Symposium at NBS in June of 1981. This Symposium will be held in coordination with the International Conference on Thermal Conductivity and the Symposium on Thermophysical Properties.

A paper, in collaboration with R. W. Armstrong (University of Maryland) titled "Analysis of Thermally Generated Microstresses in Polycrystalline Be Due to BeO Inclusions" was delivered at the Thermal Expansion Symposium and will be published in the proceedings of the Symposium. This paper resulted from the concern for the long-term stability of beryllium used in gyroscopes where BeO is a naturally occuring impurity. Because of the mismatch in thermal expansion, cooling of only 200 °C could develop microstresses around a BeO inclusion in a Be matrix that are equal to the yield stress of the Be matrix and cooling over about 400 °C would be sufficient to generate microstresses of the magnitude of the fracture stress. Also, the plastic zone around a BeO inclusion is expected to be as large as ten times the radius of the inclusion. These results have very important implications on the mechanical stability and physical properties of Be containing BeO inclusions.

Consultations continue to be offered to people trying to resolve measurement problems or needing information on thermal expansion. Support of ASTM activities in thermal expansion is also provided.

PROPERTIES, STRUCTURE, AND STANDARDS FOR GLASS AND OPTICAL MATERIALS
Task 12154

The objective of this work is to develop techniques for synthesizing glasses and crystalline solids of special compositions, shapes, structures, and properties; to propose and improve methods for the measurement of chemical and physical properties of glasses and crystals in bulk and in thin film form (e.g., solubility in and evaporation of certain elements from solid and liquid glasses; homogeneity and purity of amorphous films); to study relationships between properties, structure, and constitution; to assist the glass, and optics industries; to provide standard reference materials of use to glass-related and other industries; to characterize glass and crystalline materials for use as optical components and solid state electrodes; in particular, to measure refractive index and its change with temperature and pressure, to use Raman spectroscopy for the analysis of crystals and thin films, and to apply light scattering and microwave loss techniques to the detection of surface imperfections.

Vaporization from Glass Melts
Subtask 1 of Task 12154

D. M. Sanders, J. T. Wenzel, W. K. Haller

The stirrable high temperature transpirator continues to be an important tool in the study of vapor pressures over glass melts. It was developed at NBS several years ago and is the only existing apparatus of its kind. It allows the measurement of vapor densities under true equilibrium conditions in inert and reactive atmospheres. It can be used with incongruently evaporating melts under stirred and non-stirred conditions. Other techniques used in the project are mass-spectrometric analysis of species from non-stirred melts, weight loss studies on non-stirred melts, and analyses of surface composition profiles. These techniques are necessary to supplement the information from the stirrable transpirator. They also accelerate the data flow in this project which is slow because of the nature of transpiration techniques which require chemical analysis of high temperature condensates over long periods of times.

This year we worked principally on three different tasks. One was the study of a boron containing system, the other was the study of the influence of sulfur upon glass evaporation. In addition, we just started work on the alkaline earth/alkali silicate system.

Boron Containing System. The vaporization behavior of sodium borosilicate glass is of technological importance because both boron and sodium have substantial vapor pressures under industrial conditions. These vapors are corrosive to tank refractories and in addition boron loss is of concern because of its increasing scarcity. The addition of small amounts of boron to soda-lime-silica glass is being considered in spite of these potential problems because it lowers the melting and fining temperatures without changing the viscosity-temperature characteristics in the glass-forming range. This could lead to substantial savings in energy. Boron is also added as a component of glasses having superior chemical durability such as those used for medical fluid containers, glass fibers, thermal insulation, chemical lines, and laboratory instruments.

During the last year the results of an extensive study of the vaporization of molten boric oxide and sodium borosilicate glass in the presence of water vapor were analyzed. It was found that in the B_2O_3/H_2O system for low partial pressures water vapor a plot of the log of the boron pressure vs the log of the water vapor pressure was nearly linear with a slope of 1/2, while for higher water pressures the slope was 3/2. This finding was consistent with a model which predicts that HBO_2 is the predominant vapor species at low water vapor pressures and H_3BO_3 at high water vapor pressures. In contrast, no water vapor pressure dependence was observed for a sodium borosilicate glass melt being equimolar in sodium and boron. This suggests that a vapor species containing sodium and boron but not hydrogen is stable in the atmosphere above that melt. This observation is further substantiated by thermochemical calculations. A complete analysis of the vaporization behavior in both systems was submitted for publication to the Journal of the American Ceramic Society.

The Influence of Sulfur Upon Glass Evaporation. Another area of continuing study was the complex interaction of sulfur and water vapor on the vaporization behavior of soda-lime-silica glass. This study was carried out because all these substances are introduced during commercial production of window and bottle glass. The sulfur originates either as a by-product of combustion of sulfur-containing fuels or is added intentionally as a fining agent. Water vapor is a combustion product of the flames used to melt glass.

Thermodynamic calculations and experiments were carried out in collaboration with Dr. J. W. Hastie and Dr. D. W. Bonnell of the Chemical Stability and Corrosion Division (561) on pure sodium sulfate liquid under various atmospheres in a range of temperature from 1000° to 2000 °C. In the presence of water vapor, sodium hydroxide was the predominant sodium species.

Two experimental programs were carried out to determine the accuracy of these predictions. In the first, the stirrable transpiration apparatus (STA) was used to determine the influence of water vapor pressure on the sodium vapor density over pure sodium sulfate liquid at 1200 °C. The thermodynamic calculations predict an eight-fold increase in the sodium pressure as the water vapor pressure increases from zero to 21 Torr. This increase was not observed experimentally. A second experiment was carried out with the transpiration mass spectrometer (TMS). In this case an attempt was made to observe directly the vapor species present over a sodium sulfate liquid under the dry and wet conditions used for the STA experiment. Again no dependence was found for the sodium vapor pressure as a function of the water vapor pressure. Also, no sodium hydroxide gas was observed.

In order to shed some light on this problem, an attempt was made to find an intermediate reaction species which would lead to the calculated water vapor dependence for the vapor pressure of sodium. It was found that small amounts of sodium hydroxide added to the sodium sulfate provided such an intermediate causing the sodium sulfate to vaporize much more rapidly and to show an increase in vaporization rate with an increase in water vapor pressure. This small amount of added sodium hydroxide was not depleted during the vaporization process, but rather served to convert the sodium sulfate to sodium hydroxide vapor. This observation was verified using the TMS, where sodium hydroxide vapor was observed until the complete depletion of all of the sodium sulfate sample. We conclude from these results that a kinetic barrier exists for the formation of sodium hydroxide vapor from the reaction of sodium sulfate with water vapor. This barrier may not exist, however, under the complex conditions found in commercial glass-melting operations. The results of these investigations have been submitted for publication in the Journal of the American Ceramic Society.

The Strontium-Potassium-Silicate System. Future studies in glass vaporization are planned for the strontium-potassium-silicate system. This system is of theoretical importance in the verification of a recently developed multi-component diffusion theory. In collaboration with Dr. A. Cooper at Case Western Reserve University, an attempt will be made to measure activity data in this system. The actual experimental work will be done by one of Dr. Cooper's students under the supervision of Dr. J. T. Wenzel or Dr. D. M. Sanders.

Other Chemical and Physical Properties of Glass
Subtask 2 of Task 12154

D. J. Cronin, W. K. Haller, D. H. Blackbrun, J. T. Wenzel, D. A. Kauffman

Nucleation Kinetics in Lithium Silicate Glasses. Nucleation processes are of interest in glass because it is the absence of nucleation and/or inhibited crystal growth which allows glass formation. Furthermore, glass-ceramic materials require controlled nucleation and crystal growth for their synthesis. A study of the nucleation kinetics of lithium disilicate glass as a function of platinum concentration has been started to help elucidate the heterogeneous nucleation mechanisms in glass in general and specifically to investigate the apparent anomalous nucleation behavior when using platinum as a catalyst. Information in the literature shows there is one concentration of platinum which is most effective in bringing about volume crystallization. Such an effect would not be expected from nucleation theory.

Lithium disilicate glass is being studied since it is a well-characterized system and it has some practical interest as it forms the basis for several families of glass ceramics. The project is being carried out as time permits and with the partial assistance of a student during the summer (D. L. Swerdlow).

Cooling Induced Luminescence of Rare-Earth Phosphate Glass. In the process of producing a terbium phosphate glass it was observed that on casting the melt into a metal mold an intense green emission was produced. Subsequent spectroscopic measurements showed a similar effect in europium phosphate glasses though the emission is in the red portion of the spectrum thus making visual detection difficult because of the background from blackbody radiation.

An investigation has been carried out to determine the nature of the excitation mechanism. Spectra of the terbium emission show lines characteristic of terbium fluorescence. An obvious possible excitation mechanism involves excitation by the UV component of the blackbody radiation since it is observed that emission can be excited, weakly, in a room temperature sample by blackbody radiation from the furnace. However, other data suggest that this mechanism cannot account for the observed emissions. The emissions are observed only on rapid cooling of the sample never in a steady state situation.

The emissions are not sensitive to minor changes in terbium concentration; however, additions of other ions, such as cerium (but not magnesium) quench the emission on cooling but do not effect fluorescence under uv radiation at room temperature. The sensitivity to variable-valence ions suggests the possibility of a temperature dependent valency to excite the fluorescence spectra of the terbium.

Data analysis is continuing in an attempt to determine the excitation mechanism. Figure 1 shows the luminescent spectrum of the terbium phosphate melt at successive stages of thermal quenching.

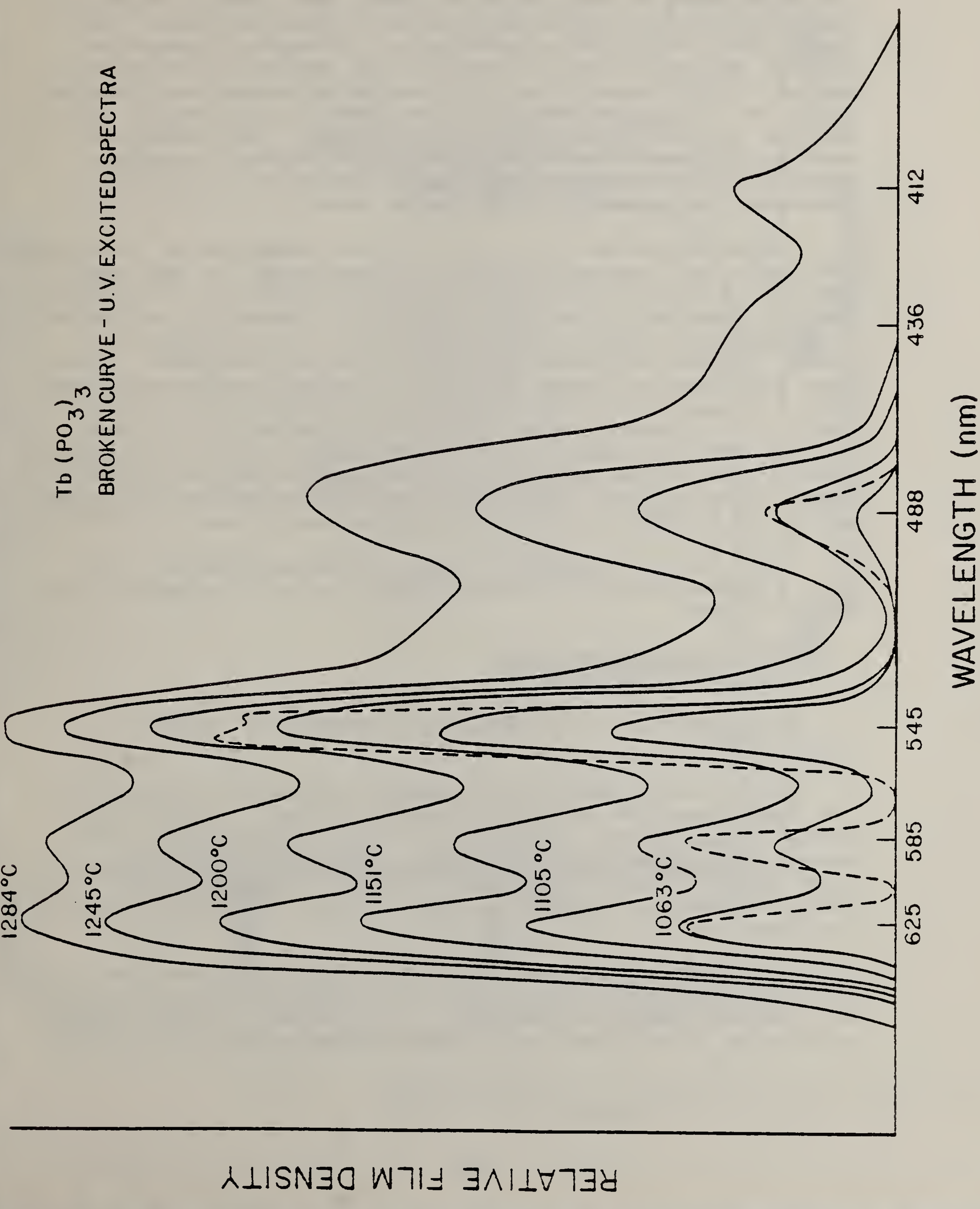
Viscosity in the MgO-CaO-Al_2O_3-SiO_2 System. This work is being carried out in collaboration with Dr. C. M. Scarfe of the Geophysical Laboratory of the Carnegie Institution of Washington and the University of Alberta. The system is of interest for a variety of reasons. It is important to geologists because it represents mixtures of two of the three minerals that form the basis of basalts. The system is also with study from the viewpoint of glass technology since it is alkali-free and stable glasses can be produced within the system. These glasses are expected to have several desirable properties such as good chemical durability and high elastic modulus and could be of commercial interest to fiber glass reinforcement of plastics, concrete, and metal. Certain glasses in the systems, those requiring low processing temperatures, might also be of interest in nuclear waste applications in the future.

Accurate viscosity data are needed for future processing considerations, to allow accurate modeling of geologic systems, and to aid analysis of melt structure studies. Results of the experiments have shown that published viscosity data on this system are considerably in error as had been suggested in the recent literature.

The viscosity data also indicate the possibility of significant structure changes occurring in the melt as MgO is replaced by Al_2O_3. Work is continuing to clarify this point.

Dynamic Synchrotron SAXS Investigation of L/L Phase-Separation. Metastable liquid/liquid phase-separations have been the subject of many studies in the past year. Due to the high viscosity of undercooled

Figure 1. Luminescence Spectrum of Terbium Phosphate Glass at Successive Stages of Thermal Quenching.



melts, the phase separation proceeds relatively slowly and can be frozen in at various stages of the process. Thus, glasses have become popular experimental models for phase separation in condensed systems in general.

Although the use of such glass systems has greatly contributed to the understanding of phase separation, there remain several theoretical questions concerning the very early stages of phase separation. Techniques which yield detailed morphological information (Transmission Electron Microscopy) have, in the past, been applied only to quenched samples. Dynamic observation of xray scattering patterns during cooling into a miscibility gap have so far been hampered by the need for long exposure during which devitrification interferes. Such observation would give information about the decomposition process in a regime where theoretical predictions are simplest and reflect the underlying fundamental thermodynamics in the clearest manner.

The recent availability of very high xray intensities at synchrotron ring facilities, promises reductions in exposure time for small angle xray scatter analysis. In a collaborative effort with G. B. Stephenson and A. I. Bienstock of the Stanford Synchrotron Laboratory, we plan to investigate early stages of phase separation in the Na_2O-B_2O_3-SiO_2 system. If necessary, other systems will also be investigated. Preliminary experiments with phase separation and quenched samples were undertaken. It appears that with the present position sensitive scintillation detector array features around 100 Å will be detectable in a minimum counting time of one second. For features smaller than 100 Å, the scatter intensity was too low for efficient counting and background resolution. Figure 2 shows a plot of count rate versus detector position for a glass sample with a characteristic phase-separation domain dimension of 350 Å.

Work in the near future will consist of the construction of our on-line sample furnace (platinum strip type) and in improvements in the counting system.

<u>Glassy Multicomponent Films</u>
<u>Subtask 3 of Task 12154</u>

D. M. Sanders, E. N. Farabaugh, M. E. Wilke (S. A. Hurwitz, R. Rodriquez)

In this fiscal year we have continued to construct a facility for the vapor deposition and *in situ* analysis of films. The system has several unique features. It has the ability to codeposit films from several atomic beams with independently variable beam intensities. After deposition, the films can be transferred, *in vacuo*, into an analysis chamber and subjected to a wide variety of instrumental analysis techniques.

The system was specifically created to produce noncrystalline films over a wide spectrum of compositions. It furthermore allows the production of films with composition gradients. It is planned to be used in general with studies of the glass structure and in investigations of thin films

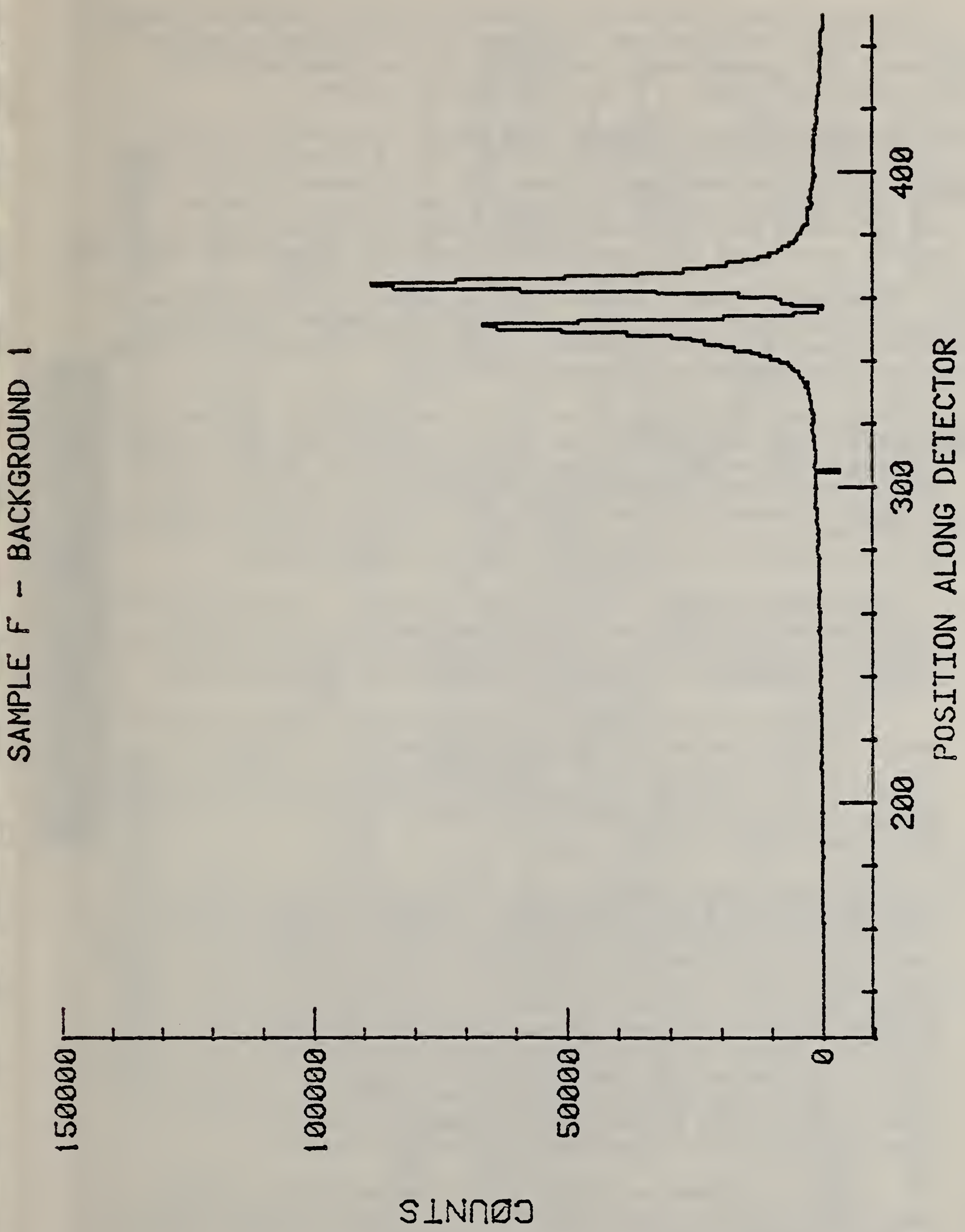


Figure 2. Synchrotron SAXS of Microphase Separated Glass of 330 Å Characteristic Dimension

in application where the absence of crystalline grain boundaries promises to have particular advantages. A schematic of the system is shown in figure 3. In the past year, the facility has been made operational, although several parts of it still have to be acquired.

Non-Crystalline Optical Coatings. One area of our glassy film work deals with the synthesis of optical films which are free of grain boundaries found in the usual optical coatings. It is hoped that such films will show improved superior resistance to intense laser radiation. This work is carried out in cooperation with Lawrence Livermore Laboratories. Results of this work will also be important to optical waveguide technology.

Homogeneous films of MgO and MgO-SiO_2 composition were produced by codeposition from separate MgO and SiO_2 molecular beams. The source materials were electronbeam heated. The deposition rates were monitored by individual quartz crystal thickness monitors.

Using xray diffraction techniques, it was shown that the degree of crystallinity of the MgO films was dependent on substrate temperature and also on the amount of a glass-forming constitutent (SiO_2). Polycrystalline MgO films could be made amorphous by the addition of as little as 25 percent SiO_2 during film deposition. Proceeding forward at the same time is the study of different substrate cleaning techniques which are essential if high quality films are to be produced.

BK-7 glass substrates were subjected to various cleaning procedures before loading into the deposition chamber loadlock. Once in the loadlock they were cleaned by a glow discharge, moved to the deposition position, and heated to the desired temperature prior to deposition.

Substrates were characterized by Electron Spectroscopy for Chemical Analysis (ESCA) after every stage of the preparation procedure, in order to evaluate the ability of these cleaning steps to remove surface contamination. Characterization by ESCA demonstrated that the hydrocarbon residue was removed from substrates by cleaning with a glow discharge for one and one-half hours.

Thin Film Stress Corrosion. During the last year an attempt has been made to identify the stressrelated reactions leading to delayed fracture phenomena in ceramic materials. In this study ceramic films are prepared by physical vapor deposition in an ultrahigh vacuum environments, subjected to varying levels of stress by deflecting their substrates, exposed to well-defined amounts of corrosive atmospheres such as water vapor, and analyzed for resulting reactions using the surface analysis techniques available in the thin film facility. These include Electron Spectroscopy for Chemical Analysis, Secondary Ion Mass Spectroscopy, Ion Scattering Spectroscopy, and Auger Electron Spectroscopy. It is hoped that in this program the stress-enhanced reactions which lead to delayed fracture in ceramic materials can be identified.

In order to determine which ceramic system-analytical technique combinations have the highest probability for observing stress-enhanced chemical reactions, single crystals of wide variety of ceramic materials

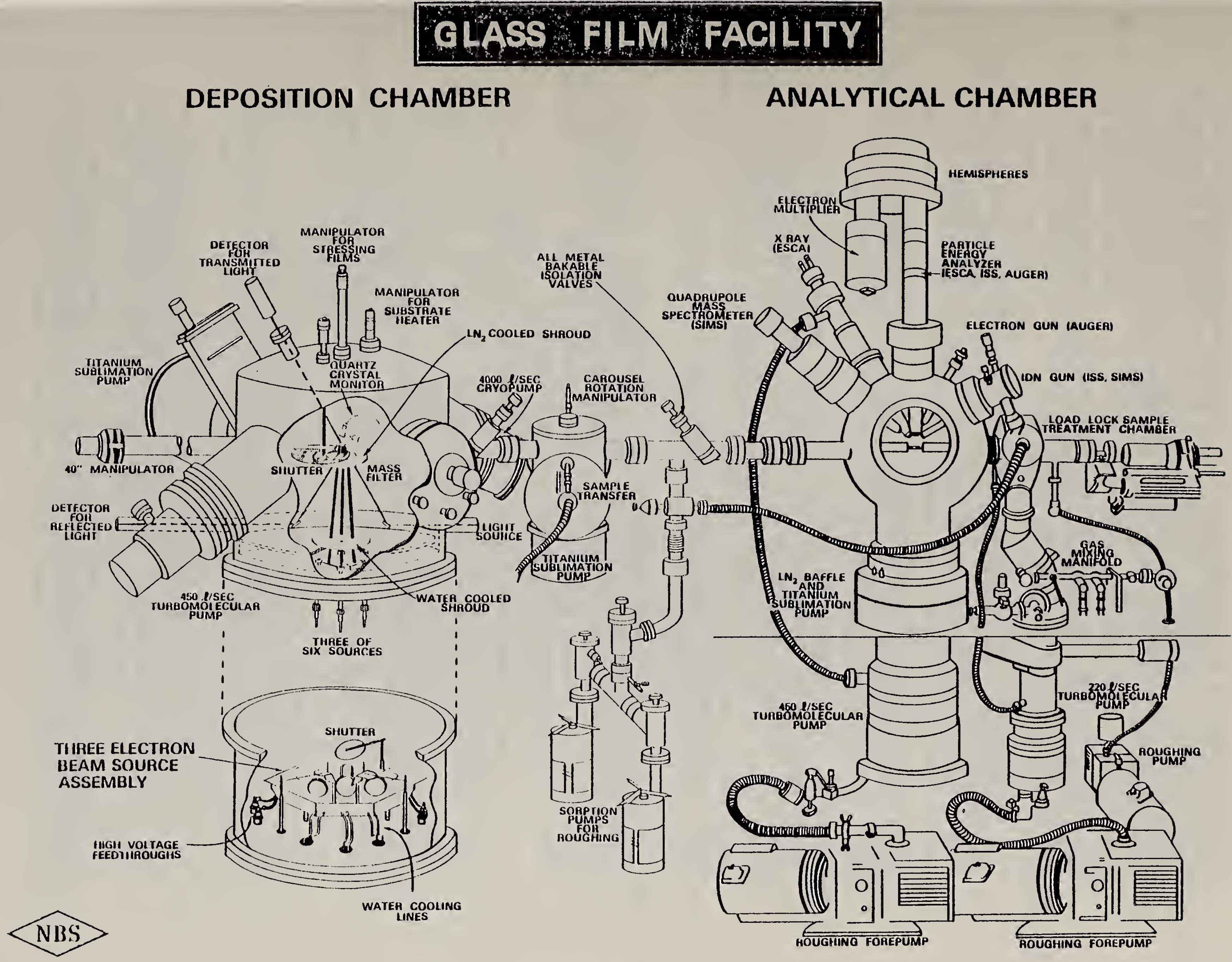


Figure 3. Schematic of Glassy Film Synthesis and Analysis System.

will be scratched and analyzed under ultrahigh vacuum conditions to characterize the unreacted surface. The pristine surfaces produced by the scratching procedure can then be reacted in a welldefined manner using a doser developed at the National Bureau of Standards by the Surface Analysis Division. The ceramic composition, analysis technique combinations which show the greatest promise will then be prepared in the thin film form for the stressrelated reaction studies described in the last paragraph. This work is being carred out in conjunction with the Fracture and Deformation Division (562).

Protective Films on Metals. Most non-noble metals, when exposed to the atmosphere, acquire a film of metal oxides or hydroxides. In some metals such as aluminum or stainless steel, such films protect the metals from further corrosion by water or the atmosphere. It has been found that most of the good passivating films are amorphous in nature and it was speculated that it is the absence of grain boundary diffusion which makes these films superior to polycrystalline films.

While it is useful for a film to have an amorphous structure, it is not necessarily sufficient. For example, the silicon dioxide films formed by thermal oxidation of silicon form effective diffusion barriers while films of silicon dioxide prepared by physical vapor deposition do not appear to be effective in inhibiting corrosion. It has been suggested that the existence of strong short-range-order in the former case may explain this difference in protective behavior.

An alternative explanation involves a difference in the density of a passive film compared to its non-passive counterpart. Other factors could be the anisotropic compressive stresses produced by "stuffing" new atoms into the surface structure and the presence of chemically combined water normally found in the passive film structures.

In order to shed some light on this problem we propose to deposit iron-chromium alloy films in the range from 0 to 24 mass percent Cr on iron substrates using our deposition system. By codeposition, we can vary the film concentration over this range in small increments and analyze the resulting metallic films in the Surface Analysis Facility prior to exposure to oxidizing conditions. We then plan to oxidize these films with varying amounts of water vapor to determine the influence of water vapor content on the passivation nature of these films. The variation of oxide film composition as well as the presence of water vapor are parameters which have potential effect both on the structure and the passivation characteristics of the films. We can also oxidize the films electro- chemically and compare those films with the ones formed by straightforward thermal oxidation.

The resulting films can then be characterized using the Surface Analysis Facility for the nature of the bonding in the passive films, the composition of those films (including hydrogen content), and the change in that composition as a function of distance from the surface of the film. We plan to determine the degree of ordering of the films using electron diffraction by depositing the films on electrochemically thinned substrates.

Finally, the films will be characterized as to their ability to protect the highly reactive iron substrate using electrochemical techniques. A correlation will be made between the film structures produced by different methods of preparation and the ability of the films to protect the substrate.

These experiments can then be repeated by directly depositing oxide compositions (for instance, iron and chromium oxides) using electron beam coevaporation. We can then correlate the structures of the resulting films with the ability of these films to protect the substrate. As before, we will have a series of films prepared in different ways, with presumably different structures which can be correlated with their passivation characteristics.

From these studies we hope to determine those characteristics which are critical in the formation of passive films and, in addition, identify possible alloying agents which increase the effectiveness of passive films. If, for instance, we find amorphous films having strong local ordering to be characteristically more effective passivation agents than their polycrystalline counterparts, we would find alloying agents which can be added to the metal in small quantities to produce such superior amorphous passivation films.

The above described project has recently been initiated. Preliminary to the production of actual films, we are presently practicing the evaluation of protective films by electrochemical means on metal pieces having the configuration of the future film targets. This project will be carried out in cooperation with the Chemical Stability and Corrosion Division (561).

Standard Reference Materials for the Glass Industry
Subtask 4 of Task 12154

M. J. Cellarosi, D. J. Cronin, W. K. Haller

Glass Liquidus Temperature SRM. The certificate for this SRM was published this year, and the soda-lime-silica glass representing the standard (SRM 773) is now on sale. This standard was developed in the past years and a full description of its nature and uses can be found in previous reports.

This SRM is especially important to the glass industry for checking test methods and to calibrate equipment for the determination of the Liquidus Temperature of Glass by the ASTM C829 Gradient Furnace Methods. SRM 773 will also aid industry in research and for development of new glasses. This is because devitrification is a chief factor which limits the composition range of glasses. Importantly, this standard will help energy conservation efforts through optimization of furnace, working, and annealing temperature systems.

Viscosity SRM. The viscosity of a is routinely determined in commercial production facilities as a reliable process control indicator. It is also frequently measured in the research laboratory as a parameter to be correlated with other chemical and physical properties of glasses. Viscometers are generally calibrated using standard reference glasses. Due to the wide variety of glasses used in industry, standards covering a wide range of viscosity values are included in the NBS SRM catalog. The SRM's are in most cases used once and discarded, thus requiring restocking periodically.

In the near future it will be necessary to restock one of the more popular SRM's, 710. As part of this effort a new precision melt viscometer is being constructed to assure the best possible calibrations. In fiscal year 1979, design of the viscometer was completed and equipment received was found to be satisfactory. In fiscal year 1980, the major elements of the instruments were constructed and preliminary calibration runs were performed. Silicone liquids were obtained, and the viscosity determined by Dr. J. Phillips of NBS. The liquids are to be used in the final calibration of the instrument. The furnace and temperature control part of the equipment will be built during the next fiscal year; thereafter the glass procurement process can be started.

Dielectric Constant SRM. This project was initiated on recommendation of ASTM Committee C-14.04 (Physical and Mechanical Properties of Glass).

This SRM activity is needed to upgrade, standardize, and calibrate the measuring systems for dielectric constant of glass employed by both producers and users of glass. This need was documented by a survey conducted by NBS on behalf of ASTM.

Glass, in general, as an insulating material is used extensively in electrical/electronics applications in two distinct ways:

(1) Glass is used to support and insulate components of an electrical/electronic network from each other and from ground. Examples of such applications are: envelopes for devices, substrates, windows for electromagnetic waves, encapsulation, insulation, etc.

(2) Glass is used to function as a dielectric of a capacitor.

For the first use, it is generally desirable to have the capacitance of the support as small as possible. For the second use, a high dielectric constant value is preferred so that the capacitor may be physically as small as possible.

NBS heads an ASTM task force of industrial laboratories for interlaboratory comparisons activities, for studies on techniques that increase test precision, and to develop standard methods.

During FY 1979, sets of measurements were carried out with glass SRM 711 samples, and procedures proposed and distributed by NBS. This activity is now in progress with more laboratories expected to gear up for participation. Thus far, the agreement in the reported data is excellent with a maximum spread in the data of less than three percent.

NBS measuring techniques utilize guarded electrodes (i.e., three-terminal configuration). A new test cell/fixture was designed for this purpose to minimize errors due to inductance/resistance and stray capacitances. These techniques were accepted by ASTM for further evaluation.

SRM-Liaison. The Glass Group maintains effective relations, with the glass industry, R&D organizations, and academia concerning the progress of science and technology in the field of glass. Active participation is extended to various ASTM committees and other standards bodies.

Plans for Future SRM's. Melt Resistivity. Accurate melt resistivity data are necessary for the design and equipment specification for electric melting furnaces. With the prospect of oil and gas shortages and increasingly stringent air quality regulations electric furnaces are receiving more attention than in the past. This attention has also generated an interest in more accurate measurements of melt resistivity and hence, a consideration of an SRM for this property. In FY79, NBS conducted an ASTM round robin testing program on glass resistivity versus temperature in the molten range. NBS distributed samples of SRM 710, procedures, and performed data analyses. The results of this round robin were encouraging but not without concern, especially in the very high temperature range. Therefore, further research on procedures and methods is warranted in this area.

Melt Density. There is some interest in the glass industry in having an SRM certified for melt density. Melt density is of importance to those designing and modeling glass-melting furnaces. Melt density information, along with an assumed or measured temperature distribution, allows estimation of the nature of convection flow patterns in the tank.

Thermal Expansion Coefficient. There has been an interest expressed by members of the glass industry and university laboratories in a glass SRM having a thermal expansion coefficient in the range of 90 to 100×10^{-7}/°C, the range of the majority of commercial glasses.

Analytical Glass Standard Reference Materials
Subtask 5 of Task 12154

D. H. Blackburn, D. A. Kauffman

A large number of complex glasses were synthesized for analytical reference material purposes. These were either in the shape of blocks, fibers, or spheres, or they were cast into source blocks used for producing thin films by sputtering. The synthesis and shaping of these glasses requires extensive experience in glassforming systems and in glass technology. Glasses have become the mainstay of the NBS SRM program for analytical instrumental analysis. The following types of standard reference materials were prepared in the last year.

Glass SRM's for Small Particle Analysis. This work has had considerable impact in the development of quantitative analysis methods for electron probe microanalysis and secondary ion mass spectrometry. Past work has resulted in the issuing of Research Material for Microchemical Analysis No. 30 which consists of ten glasses in bulk form and Research Material for Microchemical Analysis No. 31 which are the same glass compositions in the form of fibers in the four to ten micron diameter range. Work is nearing completion in the issuance of 15 glasses as Standard Reference Materials for Microchemical Analysis that have a certified chemical analysis. New glasses have been developed with different matrices which contain up to 20 different elements. Stable halogen-containing glasses have also been prepared. In continuation of work which led to the development of Mineral Glasses for Microanalysis SRM 470, asbestos mineral glass analogs have been produced for the minerals anthophyllite and crocidolite. The most ideal shaped particle for microprobe analysis standards is a sphere. In the past year, new and more efficient equipment has been constructed to produce spheres from less than a micron to 50 microns diameter. Glasses, in the future, will be available in the form of cubes, fibers, or spheres. Further expansion of this work will require glasses that contain moderate amounts of uranium and thorium oxide. Due to toxicity and radiation hazards, a separate facility is to be built with an absolute filter incorporated in the ventilation system. This facility is in the planning stage and will require new glass-melting facilities as well as associated equipment needed for glass batch handling and sphere and fiber-forming apparatus. This work was done in cooperation with several groups in the Center for Analytical Chemistry.

Thin Glass Film Standards for Calibration of X-ray Fluorescence Spectrometers. One of the most promising techniques for preparing thin film calibration standards for x-ray fluorescence spectrometry has been by sputtering glass, using a focused ion beam device. Considerable work has been done using this procedure and has been described in detail in NBS/EPA Energy/Environment Reports, the latest of which is entitled: "The Development of Potential Thin Standards for Calibration of Xray Fluorescence Spectrometry." The films can be deposited on practically any desirable clean substrate such as polycarbonate, and exhibit great adherence to the substrate obviating the need for over-coating the film to ensure integrity. The ion sputtering device requires a seven-inch diameter glass disc for the target. Special glasses have been developed containing the appropriate elements of analytical interest. (See table 1.) This requires a considerable amount of experimental glass preparation since the glass must be stable and durable and contain the elements of interest in sufficient quantities for adequate fluorescence and yet not contain elements which will give interfering and overlapping lines in the x-ray spectrum.

Table 1. Composition of Six Thin Glass Films to be Used as X-ray Fluorescence Standards

	Wt Percent						
SiO_2	40	36	36	45	40	39	
Al_2O_3	10	13.5				8	
CaO	10	18	18				
Fe_3O_4	10	13.5					
Na_2O	5			35			
PbO	20		26		20		
MnO_2					10	2	
V_2O_5	5					2	
K_2O		10			10		
ZnO			20		10	8	
MgO		9				12	
Na_2SO_4				20			
TiO_2					10	5	
$NaPO_3$							30
$Al(PO_3)_3$							70
CO_2O_3						2	
CoO						2	

Glass Target (SRM 477) for Calibration of Semiconductor Energy Dispersive X-ray Spectrometers. Work has been completed on this project. A glass designated as SRM 477 will soon be available as an NBS Standard Reference Material. The glass will be issued in the form of 25 mm diameter discs which are 3 mm thick. Three hundred and fifty of these discs were prepared and delivered to the Office of Standard Reference Materials for issue. This glass target in conjunction with an annular source of ^{55}Fe and positioning apparatus (see figure 4) makes it possible to measure window absorbtion and other losses in semiconductor x-ray spectrometers. A publication in progress entitled "A Standard Technique for Measuring Window Absorbtion and Other Efficiency Losses in Semiconductor Energy Dispersive X-ray Spectrometry" will explain the procedure in detail. The test procedure is also available from the Nuclear Instruments and Detector Committee of the IEEE Nuclear Science Society, entitled Standard Test Procedures-Semiconductor X-ray Energy. The procedure is to become an ANSI/IEEE Standard and an International Electrotechnical Commission Standard. This work was coordinated at NBS by Louis Costrell for IEEE.

Thin Glass Film Standards for Analytical Electron Microscope. For the calibration of the x-ray fluorescence and energy loss modes in analytical electron microscopy, a special glass containing SiO_2, P_2O_5, CaO, Al_2O_3, MgO, and six transition element oxides was prepared in the form of a seven-inch diameter target for large scale focused-ion beam sputtering. The sputtered films will be approximately 0.5 microns thick and will be supported by a carbon film on a standard electron microscope grid. A large number of these standards can be prepared in a single sputtering cycle when using a seven-inch target thus assuring uniformity among the standard films and eliminating reproducibility problems which would be created if a number of cycles were necessary.

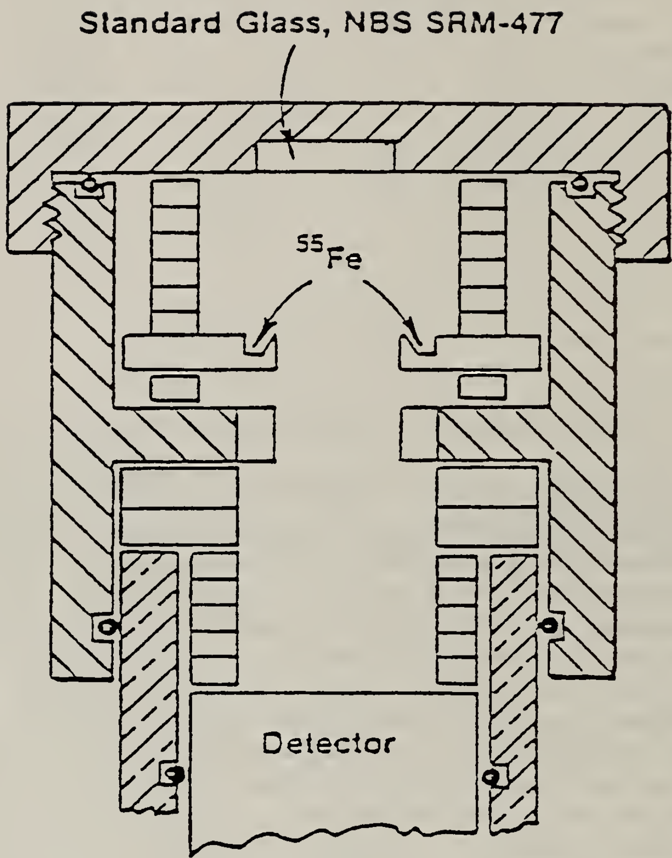


Figure 4. Apparatus for Window Thickness Measurements with a Glass Fluorescent Source.

Isotopic Glass Standards for Micro Mass Analyzers. Various sophisticated analytical instruments are capable of isotopic analysis. Instruments such as the ion microprobe analyzer and new instruments such as the Leybold Laser Microprobe Mass Analyzer and Camera Ion Microscope are all designed for mass analysis. Isotopic standards are needed for these instruments. Preliminary work has been done in the preparation of isotopic lead-silicate glass spheres. Since isotopic lead is quite expensive only gram quantities of glass will be prepared. This required a new apparatus which has been designed and constructed to produce and recover spheres from small amounts of glass. The apparatus operated successfully and spheres in the 1 to 30 micron range were produced from a lead-silicate glass prepared from natural lead oxide.

Special Glasses (Laser Glasses)
Subtask 6 of Task 12154

D. H. Blackburn, D. A. Kauffman

In continued collaboration with laser research projects at Lawrence Livermore Laboratory, glasses were prepared for the study of the fluorescence behavior of ions in a wide variety of amorphous host environments. Approximately 50 successful glasses were prepared. The glasses involved the introduction of rare earth and transition metals, in varying concentration, into different glass matrices (e.g., silicate, borate, phosphate, and telluride).

Resource Recovery and Utilization
Subtask 7 of Task 12154

M. J. Cellarosi

This project is being pursued in response to the Resource Conservation and Recovery Act of 1976. In this Act, NBS is directed to provide guidelines for the development of specifications for materials recovered from wastes.

In the area of glass, the Glass Group is carrying out cooperative activities with ASTM Committee E-38 on Resource Recovery, the glass industry, and reclamation facilities, to write test procedures, methods, and specifications for recovered glass. These activities are primarily directed toward the reuse of reclaimed glass in container manufacturing.

Container glass manufacturers use cullet (broken glass) as a percent of the charge to their furnaces. This long-established practice promotes the melting of raw materials and permits the reduction of furnace temperatures. Most of this cullet is scrap glass from the manufacturing plant itself.

A potential new source of cullet for container manufacture is the glass contained in the municipal solid waste stream. The amount of glass in this stream is estimated to be 10 to 12 percent. Most of this glass is soda-lime glass, which is the same type used for bottles and jars. Glass recovered from municipal waste is considered to offer the potentials for increasing the amount of cullet charged to the glass furnaces. The resulting benefits of such practice, would translate mainly into energy savings and extension of furnace linings life.

As of this date, several large-scale reclamation facilities have been built. Others are being constructed now, and more are planned. These facilities will separate the various components in the municipal solid waste stream. Current projections are that these plants will reclaim high quality glass, and place it in the marketplace at prices competitive with the raw materials it replaces.

During the year, NBS, ASTM, industry, and resource recovery interests have cooperated in finalizing two standards. These apply to waste glass as a raw material for the manufacture of glass containers. The standards are identified as: ASTM E708-79 (Specifications) and ASTM E688-79 (Test Methods).

Both designations refer to mixed color glass recovered by froth flotation techniques. They provide the means for determining whether the waste glass is suitable for use in manufacturing. These standards are a first step in promoting significant participation by all interested parties, especially the intended users.

The test methods combine visual examinations as well as sophisticated chemical and physical tests. These cover moisture contents, particle size, magnetic/nonmagnetic contamination, off-color glass, organic and inorganic contamination, and melt evaluations.

In FY 1979, our laboratory carried out several tests and melts on initial samples from two resource recovery plants. Results showed unacceptable quality in terms of magnetic, nonmagnetic, and inorganic contaminations. However, these results are not indicative of future production as the plants are in start-up phases and modifications are taking place to reduce contaminant levels. Especially important in this respect are efforts to reduce contamination by non-glass particles or refractories. Refractories in certain size ranges will not melt in the glass furnace. Such particles are the source of stones in the glassware and the product must be rejected for aesthetic reasons or structural weakness. The latter is an important consideration in minimizing safety hazards, especially for carbonated beverages containers.

NBS is currently cooperating in ASTM activities to develop specifications and test methods for color separated glass. The new $80 million recovery plant at Hempstead, New York, employs modules that separate glass by colors (i.e., flint, amber, and green). This is an important project as color has been identified a major barrier to recycling. The plant is projected to produce 500 to 600 tons per week of color separated glass. Oxides of iron and chromium are the main coloring agents used in glass container manufacture. For example, concentrations of Cr_2O_3 by weight percent are: 0.0015 (flint), 0.025 (amber), and 0.27 (green). Therefore, only minute quantities of amber or green colored glass can be accepted in flint.

Other NBS activities involve participation in correlation studies with actual production processes. This project was started this year, and involves a glass container manufacturing plant in Dayville, Connecticut, and the glass recovered at the Hempstead Resource Recovery facility. This work is very important in establishing firm specifications for a material which the glass industry has no prior experience with. So far, this effort has not progressed very well, mainly because of labor, technical, and environmental difficulties at the Hempstead Plant.

Optical Properties of Materials
Subtask 8 of Task 12154

A. Feldman, M. I. Bell, R. M. Waxler, M. J. Dodge

Piezo-Optics: During the past year the infrared dispersion of stress-induced birefringence has been studied in CaF_2, SrF_2, and BaF_2. We have observed, for the first time, the strain-induced splitting of the infrared-active transverse optic-phonon (IR-TO) mode of an ionic material in which the mode is Raman-forbidden. In fluorite structure materials, there exist two triply degenerate transverse-optic (TO) modes, an infrared active (IR) mode which is Raman-forbidden, and a Raman-active mode which is IR-forbidden. (This is in contrast to the zinc-blende structure in which there is a single, triply degenerate, TO mode, which is both IR- and Raman-active.) The effect of a stress on these modes is to lift the degeneracy of the modes. Until now, workers have been able to measure only the stress-induced splitting of the Raman mode but have been unable to obtain the splitting of the IR mode.

A year ago, we reported on preliminary measurements that had shown a large dispersion in the coefficients for stress-induced birefringence. This past year, we have obtained sufficient data to perform a least squares fit of the data to a strain-dependent oscillator model associated with the IR-TO phonon. In figure 5, we show the experimental data obtained, denoted by the data points, and the least squares fits, denoted by the solid curves. The fit is quite good. Notice the large dispersion. In fact, the coefficient K_{44} of CaF_2 and SrF_2 reverses sign at the longest wavelengths.

The principal conclusions of this work are:

1. The alkaline-earth fluorides CaF_2, SrF_2, and BaF_2 show a large infrared dispersion in the stress-induced birefringence.

2. The data can be fitted to a strain-dependent oscillator model associated with the infrared active TO phonon.

3. The shear deformation potentials which give the splitting of the IR-TO mode per unit strain, have been obtained.

4. The strain-induced oscillator strength anisotropy appears to be negligible.

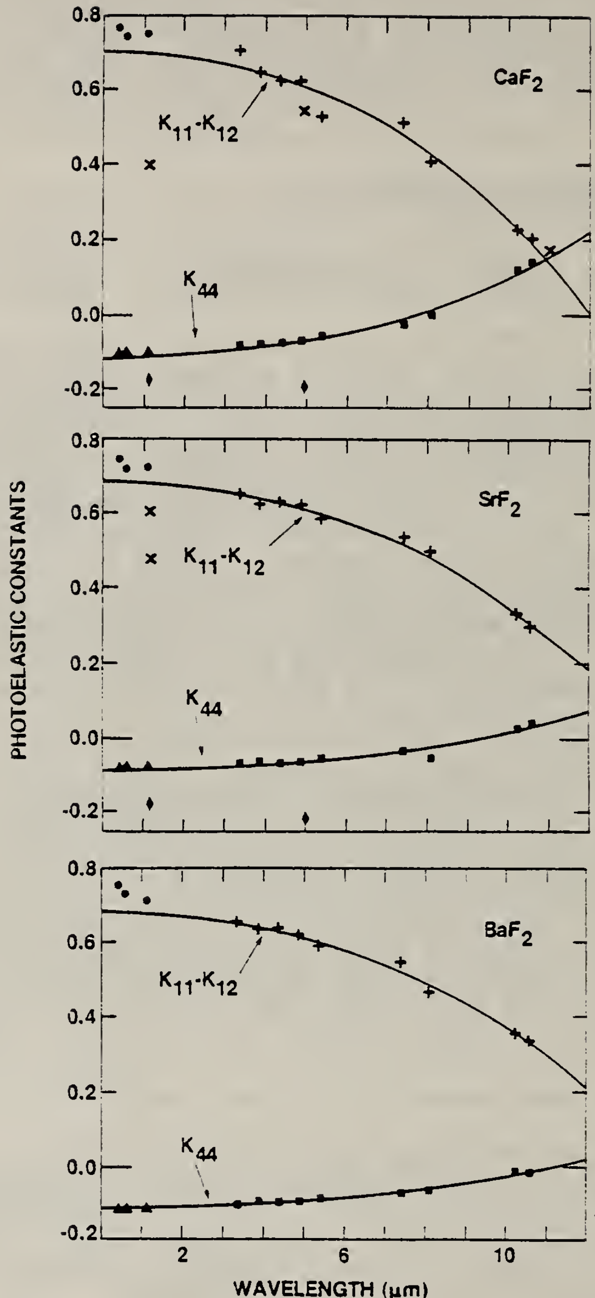


Figure 5. Photoelastic constants of CaF_2, SrF_2, and BaF_2 derived from piezo-birefringence data. The curves are least-squares fits of the data points denoted by pulses for k_{11}-k_{12} and squares for k_{44}, to a stressed-oscillator equation. The circles and triangles represent our data that were not used in the fit. The x's and diamonds are data derived from the work of others with a sign reversal on the k_{44} data to provide better agreement with our data.

5. The splittings due to [100] stress and [111] stress are of opposite signs and make contributions of opposite sign to the birefringence.

6. Comparison of the IR-TO deformation potentials with the Raman deformation potentials shows certain significant differences.

NML Topical Conference on Basic Optical Properties of Materials: A topical conference on Basic Optical Properties of Materials sponsored by the National Measurement Laboratory of NBS in cooperation with the Optical Society of America was held May 5-7, 1980. There were 122 registrants from universities, Government, and industrial research laboratories throughout the United States and more than a dozen participants from foreign countries. The purpose of the conference was to discuss the state-of-the-art in the measurement and theory of optical properties of materials of importance to advanced optical technology; that is, the conference emphasized the science of optical materials in bulk, thin film, and fiber form rather than optical devices as such.

The response of the participants to both the content and organization of the Conference was highly enthusiastic. The topical areas covered, as listed in the program were: nonlinear optical properties, ultraviolet properties, infrared properties, graded index materials, inhomogeneous materials, thin films, optical fibers, planar optical waveguides, and external influences including piezo-optics, thermo-optics, and magneto-optics. Papers dealt with many aspects of optical absorption, reflection or refraction caused by electronic and phonon transitions in different regions of the optical spectrum and how these processes are affected by external influences. A significant aspect of the Conference was the ever-increasing variety of measurement methods for characterizing optical properties. For example, new techniques, such as integrated-optics, guided-wave methods and vacuum calorimetry, and highly refined older techniques, such as spectroscopic ellipsometry and differential reflectometry, demonstrated the large advances in characterizing dielectric and metallic thin films and surfaces. The results of optical materials research will be important for many technological applications such as communications, signal processing, solar energy conversion, laser fusion, chemical spectroscopy, and optical displays.

NBS Special Publication 574 contains summaries of 62 papers presented at the Conference.

Refractive Index: Precision refractive index (RI) measurements have been made for NBS and industrial users. The final analysis of the RI data obtained for the Vee-block prisms, reported in 1979, was completed. The data were then used to calculate the tables which are necessary for the Vee-blocks to be incorporated into Vee-block refractometers used for precision refractometry. Measurements on SRM 1823, "Refractive Index-Glass," were completed and the data were turned over to OSRM for analysis and completion of the certificate. Measurements have been made on eight sucrose solutions, four samples of iso-octane, and four samples of toluene. These liquids will all be used for some type of SRM other than RI, but the RI at various temperatures and wavelengths has to be known.

Other work on refractometer test plates has been performed as necessary. A paper entitled, "Refractive Properties of Magnesium Fluoride," by Marilyn J. Dodge, was presented at the annual meeting of the Optical Society of America in Rochester, New York, October 1979.

Raman Scattering: The gradual automation of the NML Raman Spectroscopy Facility has continued, with hardware being added to the computer system as rapidly as supporting software could be developed. This year's major addition, a digital plotter, called attention to a serious weakness in the system: it's low speed in manipulating large data arrays when programmed in BASIC. Rather than give up the flexibility and ease of programming inherent in this language, we have developed a package of machine (assembler) language routines which can be invoked from BASIC and which provide capabilities for high-speed manipulation of large arrays. With these routines, many of the operations required in displaying and manipulating spectra (e.g., scaling, smoothing, background subtraction, finding sums, differences, or ratios) can be done at speeds limited only by the display hardware. These programs have aroused considerable interest among other NBS users of the Interdata 7/16 computer, and will soon be available for general distribution.

Our studies of ion implantation and annealing of semiconductors have continued in collaboration with R. A. Forman, D. R. Myers, and D. Horowitz of the Electron Devices Division. We have found that previous studies in which measurements of the local mode produced by the impurity were used to estimate the degree of electrical activation of born ions implanted into silicon were seriously compromised by failure to take into account the presence of a combination band due to the host lattice. This band coincides almost exactly with the local mode of the ^{11}B isotope, and its observation can lead to the impression that annealing has been successful when this is not the case. This problem was clearly demonstrated by comparison of the spectra of unimplanted waters with those of well-annealed samples containing ^{11}B and ^{10}B. A note describing these measurements has been prepared for submission to the Journal of Applied Physics. Another series of measurements was made in order to compare the results of laser annealing with those obtained by thermal annealing. Although the quantitative analysis of these data is not yet finished, an important qualitative result is that with proper selection of annealing conditions laser and thermal methods can yield samples with identical Raman spectra. All previous work known to us has indicated significant differences for which only tentative explanations could be offered. Examination of the annealing conditions necessary to achieve this result, correlation of the spectroscopic effects of laser annealing with the resulting surface morphology, and possible implications for semiconductor processing technology will be discussed in future publications.

In connection with studies of implantation damage, annealing, and expitaxial growth, it is important to understand the effects of strain and temperature on the lattice modes of semiconductors and on the local modes due to impurities. As a first step, a model for the anharmonic lattice dynamics of diamond-structure crystals due to Keating (with refinements by Martin, Fuller, and Bell) has been extended to include the effects of ionicity (charge transfer) which occur in the zinc-blende structure or when a donor or acceptor impurity is introduced. The model accounts well for the strain dependence of the transverse optical frequencies in all semiconductors for which experimental data are available, and these results were presented at the VIIth International Conference on Raman Spectroscopy, Ottawa, August 4-9, 1980. It appears that a very similar model can be applied to crystals having the fluorite structure, and calculations are in progress with the aim of providing a unified explanation of the results of Raman scattering measurements and those obtained by Feldman and Waxler using infrared piezo-birefringence.

A brief series of measurements was carried out in collaboration with G. Birnbaum and H. G. Sutter (Office of Nondestructive Evaluation) and M. Zoppi (University of Florence) to examine collision-induced scattering in sulfur hexafluoride at high density. In order to obtain the densities required, a system was constructed which permits operation above the critical temperature of 45.6 °C. An optical chopper and appropriate software were added to permit automatic background subtraction, and with this equipment excellent depolarized spectra were obtained in runs of 12 to 60 hours. Data were obtained over the density range of one-tenth to three times the critical density, and analysis of the density dependence of various spectral features is now in progress. An important preliminary result is that scattering in the region from 100 to 140 cm^{-1} which had previously been regarded as evidence of a failure of the first-order dipole-induced-dipole (DID) scattering model is in fact due to the presence of at least two hot bands in this region. Careful analysis will be required to eliminate the effects of these bands and provide a reliable test of the DID model.

Properties of Pyroelectrics (in cooperation with A. Shaulov, G. M. Loiacono, and W. A. Smith of Philips Laboratories): Interfacing of the microprocessor system for control of the dynamic pyroelectric response measurement system is now completed except for minor changes which may be necessary during final de-bugging of the software. An improved measurement technique designed to provide simultaneous determinations of the pyroelectric coefficient, dielectric constant, and specific heat has been devised. Preliminary tests of the method using analogue methods were only partially successful, but the approach still appears promising since a fully digital system can be expected not to suffer from problems of the type encountered in these tests.

Crystal-growth efforts at Philips Laboratories have not yet produced samples of metal-halogen boracites suitable for dielectric or Raman scattering measurements, but specific heat data have been obtained. These results exhibit an effect which we noted previously in pyroelectric coefficient and specific heat measurements in other ferroelectrics, i.e., rather than a single peak in the property of interest at the phase transition temperature, we find multiple peaks within a small temperature range in the immediate vicinity of the transition temperature. We have found strong evidence linking this behavior to inhomogeneous internal strain distributions in our samples, and demonstrated that the effect can be controlled to great extent by deliberately introducing non-uniform strains or removing them by annealing. Review of existing data, together with some new measurements, clearly showed that this behavior is most pronounced in crystals which are strongly ferroelastic, either because the phase transition is intrinsically ferroelastic or because the primary order parameter is strongly coupled to an elastic distortion. A report of these findings has been accepted for publication in Ferroelectrics.

Nondestructive Evaluation
Subtask 9 of Task 12154

A. Feldman, A. H. Kahn, G. S. White

Theoretical Modeling in Eddy Current NDE: We have examined methods for solving inversion problems by the analysis of eddy current experimental data. If we limit the investigation to simple geometries, such as a slab or a cylinder, it should be possible to use impedance measurement as a function of frequency to construct a resistivity profile of the material by examination. This inversion can be performed by a method of integral equations (known as the Gelfand-Levitan and Marchenko methods in quantum theory) and by another method of direct Fourier analysis. Both methods are now being explored for computational practicability.

In the problem of crack diagnosis by eddy current methods, there have been reports of wide variability in the signals from real and artificially produced crack or other defect specimens. Part of this variability may arise from the zone of plastic deformation in the vicinity of the crack. This plastic zone may vary in dimensions and in material parameters, according to its method of production. Initial calculations show that expected resistivity variations in the plastic zone have little effect on eddy current signals, but that possible variations in magnetic permeability, as in stainless steels, could produce a significant effect. A computational approach, based on the finite element method, is being prepared for finding the eddy current distribution in the vicinity of a crack with allowance for the variation of material parameters in the plastic zone.

Optical Nondestructive Evaluation: Optical scattering from defects is an area of importance in nondestructive evaluation. It is the purpose of our research to determine whether quantitative data, such as defect dimensions, obtainable from optical scattering data. For this purpose we have been performing both measurements and model calculations of radiation scattered from well-defined shallow grooves in metallic surfaces and have compared theory with experiment.

In the experiments, chopped 10.6 μm radiation from a 3 watt CO_2-laser was incident normal to a specimen containing a shallow rectangular groove. The specimens were prepared by scribing of grooves into an aluminum coating that had been evaporated onto glass optical flats. Two sets of specimens were used: one set of specimens was used as scribed; in the other set, the specimens were overcoated with an additional thin layer of aluminum. The groove dimensions in both specimen sets were nominally 10, 20, and 50 μm wide by 0.5 μm deep. Figure 6 shows the measured profile of a 50 μm uncoated groove.

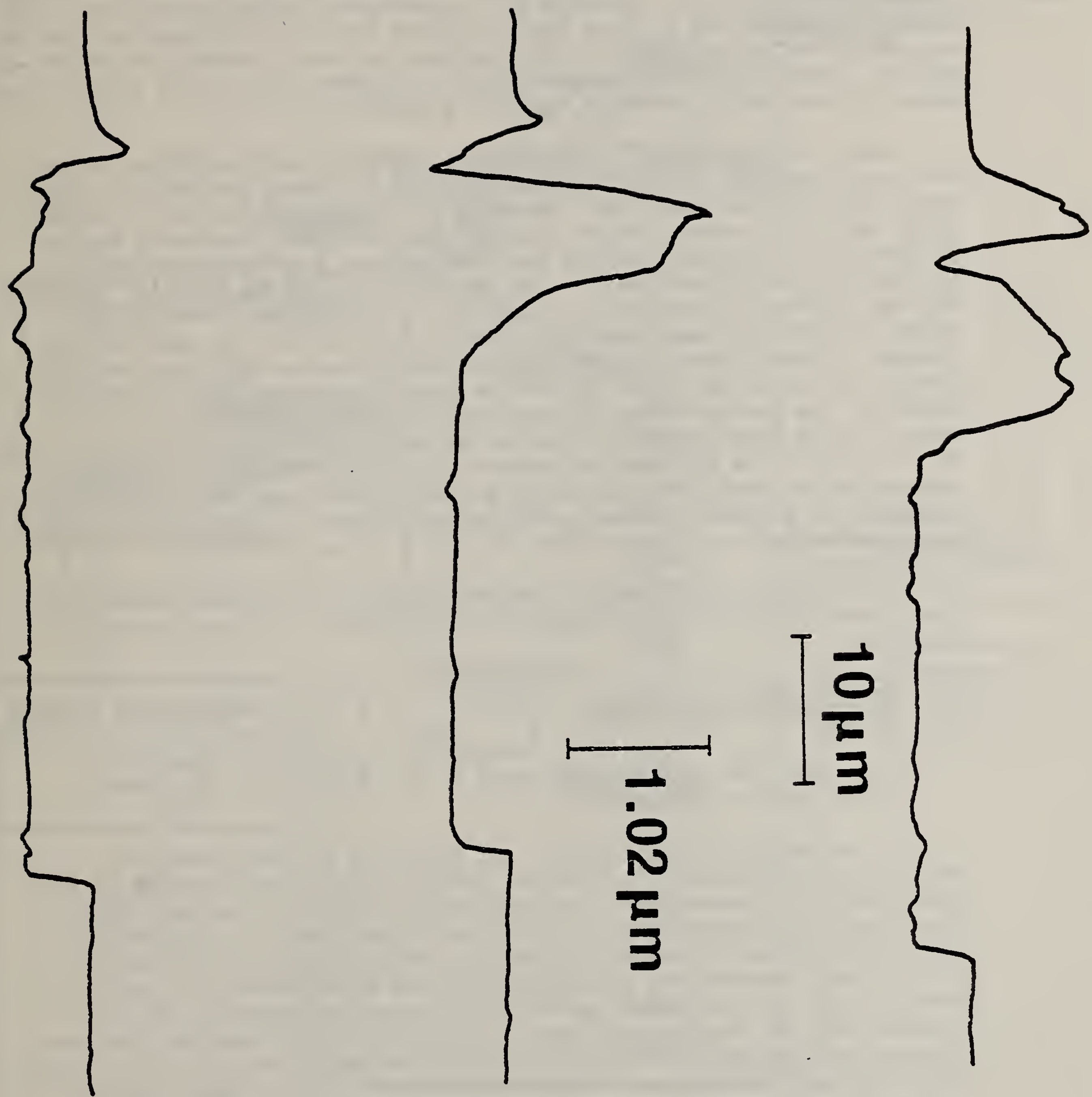


Figure 6. Upper, middle and lower cross sections of uncoated 50 µm groove measured by diamond stylus profilometer.

The use of 10.6 μm radiation has several advantages: the effect on scattering of surface microirregularities is minimized; the fabrication of well-defined grooves of dimensions comparable to the wavelength is facilitated; the far field approximation in the model calculations can be used.

A schematic diagram of the measurement apparatus is shown in figure 7. Scattered radiation was measured by a pyroelectric detector that was swung about the specimen in a plane that contained the incident beam and that was perpendicular to the groove in the specimen surface. Careful attention was paid to system alignment because certain alignment errors were shown to cause severe distortion of expected scattering patterns.

Model calculations of the expected scattering were performed on the basis of Fraunhofer diffraction theory. The following assumptions were made: the incident beam had a Gaussian intensity distribution; the beam width was significantly larger than the groove width; scattering was due to specular reflection from the specimen surface and the groove bottom but not from the groove walls. The resultant scattering function obtained was the diffraction pattern of a uniformly illuminated slit with the intensity uniformly modulated by a factor dependent on the depth of the groove. Figure 8 shows a comparison between experimentally determined scattering and an empirical fit to the data of a single slit diffraction pattern. The points denote the measured scattering intensity of a nominal 50 μm wide uncoated groove as a function of scattering angle. The solid curve is the diffraction pattern of a 52 μm wide slit. Agreement appears to be quite good. Comparable results have been obtained with some of the other grooves; however, with certain grooves, large discrepancies were observed which are attributed to groove irregularities.

Further work is planned to compare scattering from deep grooves with theory and also to study the effect of polarization on the scattering function.

<u>Energy States in Silicon</u>
Subtask 10 of Task 12154

A. H. Kahn (in collaboration with J. R. Lowney and H. S. Bennett of the Electron Devices Division)

In the design for fabrication and operation of semiconducting devices, it is necessary to know the density of electronic states of the bands and of the impurities. At high doping levels, screening effects should cause a disappearance of the bound states, and this information should be included in models for device operation and fabrication. To provide this information, we have studied the disappearance of impurity levels in silicon and germanium due to free-carrier screening of the Coulomb field of the impurity ions. The ground state eigenfunctions and eigenvalues have been calculated for electrons described by an ellipsoidal effective-mass Hamiltonian. A two-dimensional finite element analysis was used to obtain the solutions. Only moderate carrier densities (10^{19} cm^{-3} for silicon and 10^{18} cm^{-3} for germanium) are needed to cause the impurity levels to disappear into the conduction band, the result at high doping densities being simply a degenerate semiconductor.

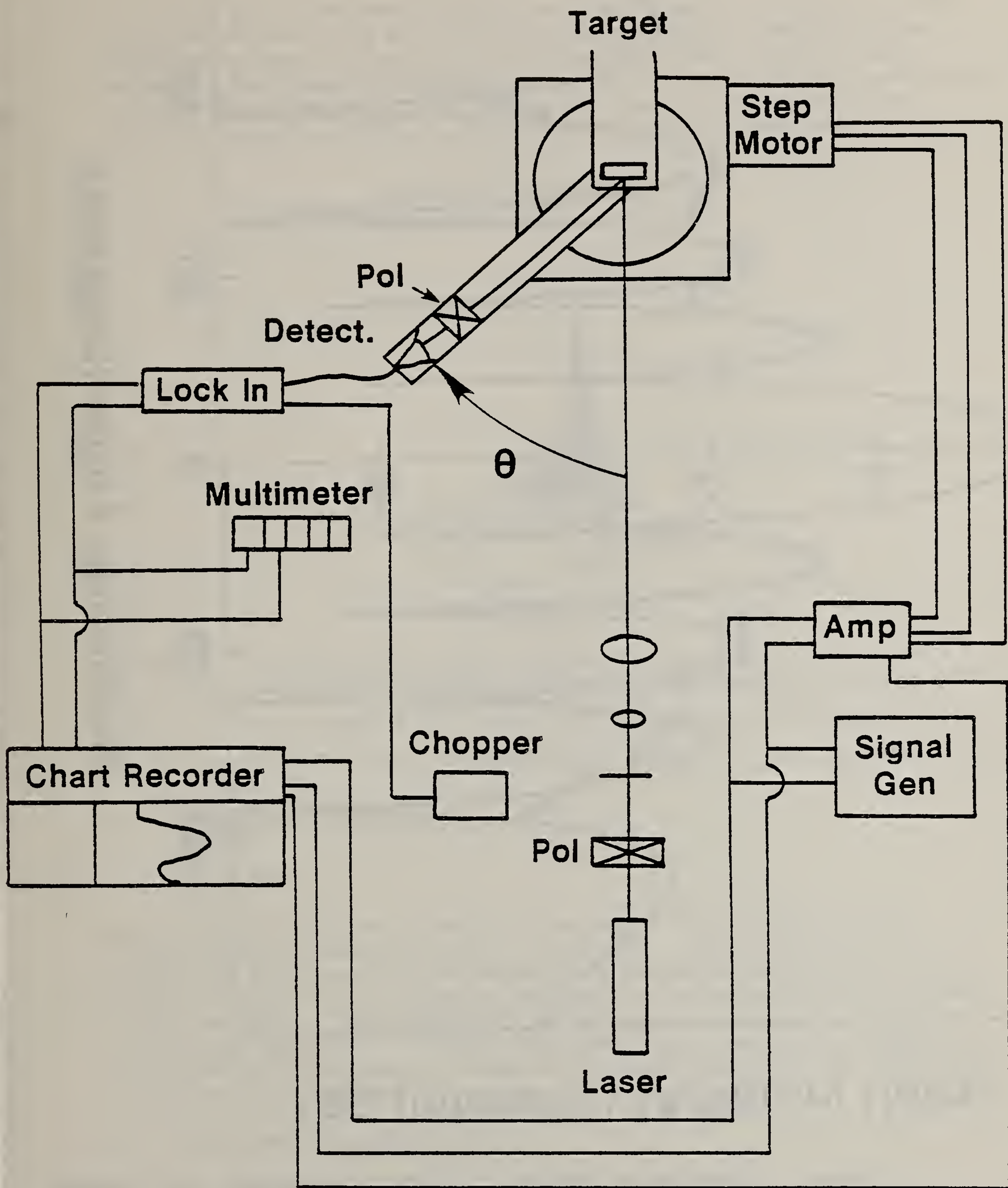


Figure 7. Schematic diagram of scattering apparatus.

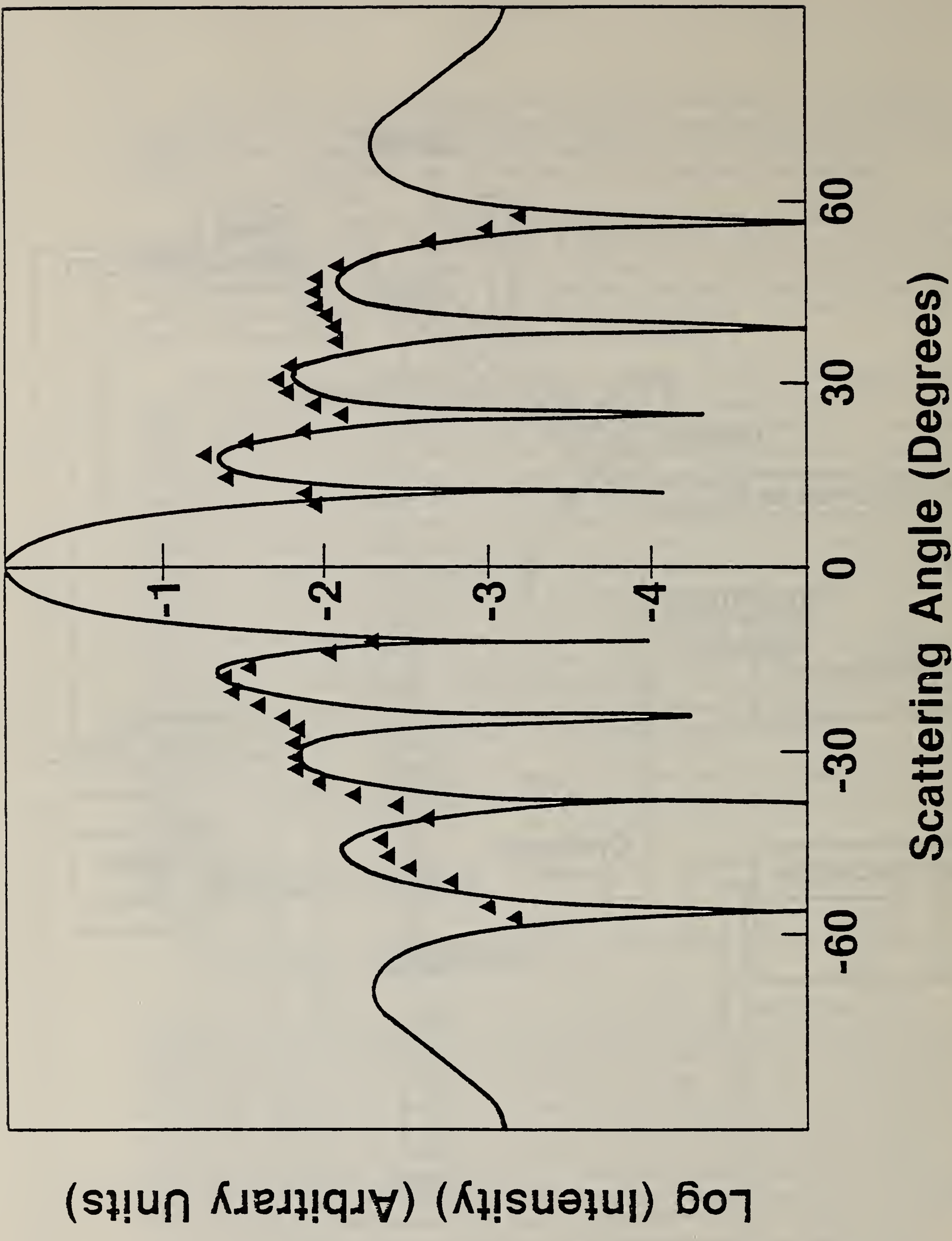


Figure 8. Logarithm of observed scattering (triangles) from uncoated 50 μm wide specimen superimposed on the calculated logarithm of a (solid) ideal single slit diffraction pattern from a 52 μm side slit.

In figure 9 we show a typical example of the silicon impurity wave function as calculated by the finite element method. Because of the anisotropic mass, cylindrical coordinates are used. For this case, screening has reduced the binding energy to 11 percent of its unscreened value. By extrapolation from similar computations, we obtained the critical screening radius at which the bound level disappears.

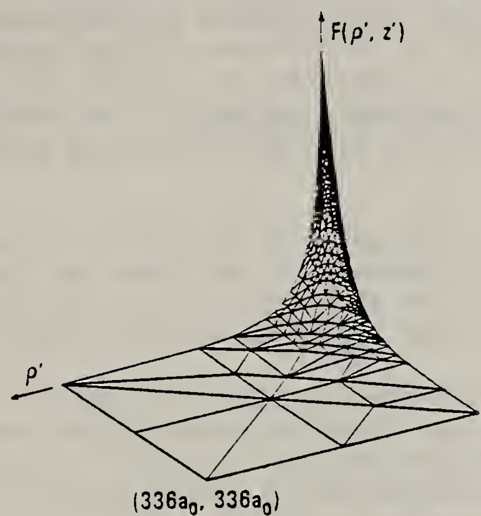


Figure 9. Display of the finite element wave function $F(\rho',z')$ for a bound donor electron in silicon with screening radius $r_s = 50\ a_o$ ($a_o = 0.529 \times 10^{-8}$ cm). With this degree of screening, the binding energy is reduced to 11 percent of the unscreened value.

Electrocatalysis
Subtask 11 of Task 12154

M. I. Cohen

These efforts are directed at the need for measurement of the electrochemical characteristics of materials. The primary effort is toward the development of automated instrumentation for both laboratory and field acquisition of data to be used for the determination of these characteristics. This program is being funded by three other agencies (DOT, EPRI, and DOE). Although each agency has a particular objective, the three are complementary, enabling a single comprehensive design for instrument construction.

The three programs consist of:

1. Federal Highway Administration - Measurement of Corrosion of Reinforcing Bars in Concrete

2. Electric Power Research Institute - Corrosion of Concentric Neutral Cable for Power Distribution

3. Department of Energy - Measurements of Electrocatalytic Characteristics of Fuel Cell Materials

All three programs are joint efforts of this Division with the Chemical Stability and Corrosion Division (561), and they will be discussed as a unit.

The instruments being developed are a direct outgrowth of the one designed previously for use with the ongoing program in electrocatalysis for fuel cells. The design has been upgraded by going to a higher performance processor (6809) which is compatible with the earlier version (6800). This change enables an improvement in speed and flexibility with minimal effects on the hardware and software already operating. This original unit, as modified, is serving not only as an operating device, but as a development system for the other systems being built. Two are under construction, one a laboratory system and the other a field unit.

The field unit (being built for DOT) is a smaller version of the lab system and is intended as a prototype for the Highway Administration. If they deem the system effective, it will be adapted to weather extremes and then duplicated and issued to various State highway departments.

The laboratory system is capable of operation identically the same as the field unit, but can also perform other operations. Software is interchangeable between the two versions. Since the hardware in each is identical, new techniques can be tested on the lab system and when perfected, transferred to the field unit.

The primary technique used at the moment in these instruments is a variation of that used in the original DOE instrument. The interfacing to the measurement board is the same, but we are doing a galvanostatic determination instead of a potentiostatic. In this technique, we measure the potential difference between the working electrode and a reference electrode due to a current impressed between the working electrode and the counter electrode. By suitable timing choices, the corrosion potential can be measured (when the polarizing current is off) at the appropriate point on the waveform to eliminate the effects of the resistivity of the surrounding electrolyte (concrete or soil depending upon which of the other programs is involved).

The education program on microprocessors in instrumentation started last year has continued. The Center for Materials Science funded another session of the basic course in the fall of 1979. A third session is being planned as is an advanced course.

The Advisory and Consultive services we have been providing are expanding. Many of the staff in the Center have taken advantage of these services, and we expect further growth. An effort is underway to organize our data files in a better fashion so that we can institute a more efficient electronic data library for Center use.

Plans

1) Delivery of field system to Federal Highway Administration at the end of the Fiscal year (October 1).

2) Completion of extended laboratory system in first quarter.

3) Hardware implementation of other techniques and associated programming.

4) Impedance techniques for fuel cell measurements, and others, will be developed.

5) Investigation of noise measurement techniques as a tool for field determination of corrosion will be implemented.

DURABILITY OF CERAMICS AND GLASS IN SERVICE ENVIRONMENTS
Task 12155

The objective of this task is to develop test methodology and collect critical data for the assessment of high temperature materials in MHD, coal gasification and gas turbine environments. The Division's activities in these areas are part of two programs that cover several Divisions of the Center for Materials Science: Data Center for Fossil Energy Materials, Materials for Coal Gasification, Structural Ceramics, and MHD Materials. All four programs are supported by the Department of Energy augmented by some NBS contributions. The work of each project is closely related to and based on the expertise of Tasks 1-4.

Data Centers for Materials and Components for Fossil Energy Applications
Subtask 1 of Task 12155

H. M. Ondik, A. Perloff, W. S. Brower with R. C. Dobbyn, W. A. Willard, I. J. Feinberg, (562)

The Fossil Energy Information System consists of two Data Centers operating cooperatively to provide a central data base of materials and components performance and properties data. One element of the system is the Materials Properties Data Center which is responsible for compiling information on construction materials for coal conversion use and MHD power generation. This Center is largely staffed by personnel from the Ceramics, Glass, and Solid State Science Division, Ondik, Brower and Perloff with Feinberg (562). The major source of the data is the Center's library of DOE materials research contractors' reports. There are between 45 and 50 DOE-funded projects generating materials properties and performance data for coal conversion and utilization and MHD powder generation. As time allows, other information sources are sought to expand the data base. Computer storage of the materials properties data base and access to it will be controlled using a commercially available data base management system so that, in time, users may have direct on-line access to search the data.

The other segment of the information system is the Failure Information Center largely staffed by members of the Fracture and Deformation Division, Dobbyn and Willard with Brower (565). The source of information consists of reports of materials and component failures submitted to DOE on a voluntary basis by the various coal conversion plants. The information is abstracted and entered into computer storage under a system allowing high speed retrieval with a variety of search schemes. One goal of the Center is to develop the file of operating experiences and correlate them so that trends will be observed indicating primary causes of plant failures for the guidance of designers and operators of coal conversion plants.

A major aim of the total information effort is to access all of the data through one Data Base Management System (DBMS). The nature and structure of the data sets of the two Centers are too different to permit storage and search of the data in one file, but the same DBMS can be utilized to control two data files so that they can be searched consecutively using the same search terms. The user can then obtain the results on a given material or performance characteristic provided both by reseach and testing programs and by in-service experience. Procurement of the DBMS and a commercial computer vendor's services has occupied a large portion of the staff efforts of the Materials Properties Data Center. After completing the technical evaluation of the written proposals submitted in response to our request for proposals, it was necessary to prepare and keyboard some 80 data sets (5,000 lines of data) and transfer these to magnetic tape for testing use of the competing vendors. A series of technical explanations to the vendors were also necessary because our data are much more complicated than the material with which most commercial vendors deal. A double series of benchmark tests were performed by each vendor, testing their handling of the data and the capabilities of their systems. A contract has been awarded and training in the design and use of the DBMS for the personnel of the two Data Centers is beginning.

The existing computer file of the Failure Information Data base contains some 500 reported failures. Although fewer pilot plants are now operating, resulting in a very slow rate of increase of the data file, there is continuing interest on the part of the user community. Some 1100 reports and about 30 data tables and abstracts summarizing in-service materials and components performance were sent out in response to over two dozen requests. An interpretive report, analyzing erosive wear failures has been published as an NBS Internal Report. Information is regularly supplied for the Failure Experiences feature of the DOE Materials and Components Newsletter, published by Battelle-Columbus.

The major effort of the two Data Centers for the past year has been the preparation of a publication, Construction Materials for Coal Gasification--Performance and Properties Data, currently submitted to DOE for approval. This book contains information gained in practical plant experience and also the results of materials research and testing programs. It deals with the information in the context of eleven separate component areas of coal gasification plants, and draws from this information an indication of possible candidate materials of contruction. A separate section of the Handbook includes extended data for the chemical, physical, and mechanical properties of the candidate materials. The book will consist of loose-leaf pages so that increasing and revising the data can be done readily on a regular basis.

Chemical Degradation of Ceramics: Reactions and Transformations
Subtask 2 of Task 12155

F. A. Mauer, C. R. Robbins

The investigation of castable refractories for coal gasification applications in support of flexural strength measurements (see Task 12122) has been completed. Both conventional and in situ powder diffraction analysis methods were used to determine the chemical response of test specimens to environments intended to simulate initial start up and operation of a gasification reactor. Some results of an optical microscopy, SEM, and powder diffraction analysis of approximately forty core samples from the refractory lining of the Conoco Lignite Gasification Pilot Plant in Rapid City, SD, were also included in an attempt to correlate short term *in situ* test data with the effects of much longer exposure (3/4 year) under actual service conditions (0.9 MPa and 843 °C). The following two paragraphs are from the summary of the final report (NBSIR 80-2064).

"The *in situ* x-ray studies have shown that, in the presence of steam and with changes in temperature, a high purity castable refractory is subjected to frequent changes in bonding phases and to intervals in which the main bonding phase is in a state of transition. These changes are undesirable and should be minimized by avoiding exposure of the refractories to steam below 750 °C, or preferably 900 °C. Reaction of the high purity refractory with steam containing alkalis and silica from impurities in the coal should be expected to occur at the working face with formation of various silicates. These may alter the course of hydration/dehydration reactions and the formation of bonding phases.

"The CaO-Al_2O_3-SiO_2 refractory has been shown (Task 12122) to increase markedly in flexural strength with exposure to either simulated or pilot plant gasification atmospheres. The increase in strength is attributed to the formation of CAS_2 and A_3S_2. Once formed, these compounds are not subject to hydration/dehydration and are stable in steam over a large temperature range. Leaching of silica and other components from this type of refractory has been observed, but may not pose a serious problem during the service life of the material."

Slag Viscosity
Subtask 3 of Task 12155

W. S. Brower, J. L. Waring

Viscosity measurements have been made on two synthetic slag compositions over a range of elevated temperatures at steam pressures up to ~ 100 psi. The compositions of the two synthetic slags were quite different in respect to their alkali content, one was high, ~ 20 wt %, the other much lower ~ 5 wt %. These slags were modeled to represent a high alkali western coal residue and lower alkali eastern coal residue. The high alkali composition exhibited an increase in viscosity with increasing steam pressure, whereas the lower alkali composition exhibited a decrease in viscosity with increasing steam pressure. The viscosity behavior of the high alkali slag was unexpected, the low alkali slag behaved in manner more consistent with conventional glass technology. A summary report has been prepared and submitted for publication.

High-Temperature Applications of Structural Ceramics: Kinetics of Oxidation
Subtask 4 of Task 12155

F. A. Mauer, C. R. Robbins, T. A. Hahn

Under an interagency agreement with the Department of Energy signed in January 1980 research is being conducted by NBS under four projects (see Task 12122). A principal factor affecting the mechanical performance of silicon carbide, silicon nitride, sialon, and other structural ceramics in high temperature applications is their ability to remain stable in atmospheres having a wide range of oxygen partial pressures. The objective of this subtask is to identify the crystalline phases formed under well-defined oxidation conditions in the interior and in the surface of various structural ceramics and to determine the factors that effect oxidation kinetics. The information will be used in explaining the degradation of mechanical properties at elevated temperatures. The method involves x-ray analysis of specimens before and after high temperature fracture tests and crack growth tests (Task 12122), as well as specimens exposed in a laboratory furnace in controlled atmospheres. To date, the pre-test analysis of a set of nine sialon specimens of compositions represented by $Si_{6-Z}\ Al_Z\ O_Z\ N_{8-Z}$ (where Z = 1, 1.3, 2.3, and 3) has been completed. The samples which will be used for fracture and crack growth tests were prepared by Kazuo Kobayashi of the National Industrial Research Institute of Kyushu, Japan. Another group of twenty-three specimens prepared in the Laboratory of Professor Tien at the University of Michigan is now being analyzed. These specimens, which will be used in notched bend fracture tests, have a refractory garnet grain boundary phase intended to reduce the high temperature creep characteristic of materials with a glassy intergranual phase.

Thermochemical Data for Structural Ceramics
Subtask 5 of Task 12155

J. L. Waring, R. S. Roth, H. S. Parker (M. C. Austin)

This project is part of a Center-wide program funded by DOE on structural ceramics (Si_3N_4, SiC) for gas-turbines. The purpose of this work is to improve the understanding of the mechanical behavior of structural ceramics and to provide essential data on refractory materials used in fossil energy systems. As part of the program, a study (ongoing for about six months) is being conducted to determine the relationship between thermodynamic, thermochemical properties, microstructure, and mechanical properties of silicon nitride and silicon carbide based materials. In addition studies are being conducted to improve the properties of these materials by controlling compound formation, melting, decomposition, and phase changes during use.

In the past the work of this group has been concerned primarily with oxygen-based systems. The increasing emphasis on nitrogen-based ceramics has necessitated considerable modification of existing equipment and installation of new equipment to provide heating and characterization of specimens under controlled conditions of atmosphere, temperature, and pressure. Equipment now in use can provide for heating of bulk samples at temperatures as high as 2400 °C, pressures to 300 psi, and partial pressures of oxygen as low as 10^{-24} atmosphere. Characterization by high temperature x-ray, in controlled atmosphere, to temperatures in excess of 1600 °C is also possible.

The thermodynamics of the so-called $\alpha \leftrightarrow \beta$ transition in Si_3N_4 was investigated in the high temperature x-ray furnace. The hexagonal c-axis of β-Si_3N_4 varied from about 2.911 A at room temperature to about 2.924 A at 1410 C and the a-axis varied from about 7.616 A at room temperature to 7.644 A at 1410 C. The dissociation temperature of Si_3N_4 in small sealed Mo tubes appears to occur between 1925 °C and 1950 °C. This is the temperature at which the dissociation of Si_3N_4 into N_2 gas and Si liquid has become so rapid that the experiments can no longer be continued in a sealed tube for a practical length of time.

The formation of the x_1 phase along the join Si_3N_4:$2SiO_2$:$3Al_2O_3$ (mullite) has been reported to cause the loss of mechanical strength in structural Si_3N_4 bodies. X-ray diffraction patterns of all the specimens prepared showed primarily x_1 with a trace of mullite and (α and β)-Si_3N_4. Single phase x_1 was not obtained and more work is needed to properly characterize the x_1 phase.

Several attempts were made to grow single crystals of the β-Si_3N_4 phase in a horizontal resistance furnace. High purity (99.99 percent) silicon was heated in purified argon atmosphere to $\sim$ 1450 °C. At this point, forming gas (95 percent N_2/5 percent H_2) was admitted to the growth chamber with a 10:1 mass flow ratio A/N, maintained for 24 hours and cooled in pure argon. Many small prismatic crystals of β-Si_3N_4 (up to 0.5 mm in length) had formed on the surface of the silicon with some glass and SiC crystals. Further experiments to eliminate glass and carbide formation are in progress.

Thermochemistry of Slag
Subtask 6 of Task 12155

L. P. Cook

Phase equilibrium investigations into the high temperature behavior of potassium-bearing coal slag, similar to that which is found in MHD systems, were resumed. This work has been directed along two lines: (1) determination of the major chemical distinctions between seven-component slags produced by combustion of "eastern" and "western" coals; and (2) a more in-depth study of the phase equilibrium properties of the potassium-rich part of the system K_2O-CaO-Al_2O_3-SiO_2.

A paper presented at the 7th international MHD conference held June 1980 at MIT described the first series of results of multi-component modeling of synthetic K_2O-bearing slags. Relatively small differences in bulk chemistry (particularly CaO/FeO_x) were shown to have dramatic effects on the phase equilibrium behavior of such slags. Oxidation effects were shown to be particularly important from a theoretical point of view, especially in determining type and degree of melt polymerization. Further research in the seven component K_2O-CaO-MgO-FeO_x-Al_2O_3-SiO_2 system will focus on determining the nature (P-T-X properties) of the high temperature two-liquid field observed in the "eastern" slag. An attempt will be made to develop solution models--probably based on melt polymerization theory--which adequately describe this behavior. Separation of an iron-rich liquid in such slags under MHD conditions could conceivably affect generator performance.

Phase equilibria in the sytem K_2O-CaO-Al_2O_3-SiO_2, a simplified model system for "western" MHD slags, have proved to be more complex than thought. Research in this system has brought to light features of potential significance for K_2CO_3 seed recovery, in particular: (1) The difficulty with which CO_2 is removed from K_2SiO_3 and $KAlO_2$-rich compositions, and (2) the tendency for anomalous melting in the subsystem K_2CO_3-$KAlO_2$. Experimental results suggest that a substantial amount of K_2CO_3 may be held dissolved in slag solutions rather than forming a well-defined, readily separable carbonate phase. In the system K_2CO_3-$KAlO_2$, compositions with a high percentage of K_2CO_3 may be held for 400 °C above the fusion temperature of K_2CO_3 and yet show no sign of melting. Such potassium carbonate/aluminate mixtures are thought possibly to form partially ordered liquids (mesomorphic phases), thus leading to unusually high viscosity resembling that of a solid. A paper describing these results was presented at the Conference on Ceramic Interfaces held at Berkeley in July 1980. Other experiments in K_2O-CaO-Al_2O_3-SiO_2 have pointed to the existence of what may be new quaternary phases. These experiments have also reaffirmed the relatively high stability of the CaO-$KAlO_2$-SiO_2 subsystem, a major chemical divide within the quaternary system, on opposite sides of which lie melts with markedly different properties. As these phase equilibrium studies progress, correlation with the potassium vapor pressure measurements completed in Division 561 is done through a collaborative effort at modeling liquid/solid/vapor equilibrium relations. New data have so far reaffirmed the tendency for additions of CaO to reduce the activity of K_2O to a degree well beyond the proportions involved.

<u>Electrical Conductivity and Polarization Effects in Coal Slag</u>
Subtask 7 of Task 12155

W. R. Hosler

The most abundant material likely to be found in the duct wall of an MHD generator is coal slag and this must pass all the generated current in the transverse direction. The electrical conductivity of this complex substance is not well understood. While electrode and insulator materials have been studied also, the main emphasis is to obtain a thorough understanding of the slag conductivity process. These studies include the relationships of the charge transport mechanism to temperature, oxygen partial pressure, slag elemental components and chemistry, and previous treatment with respect to temperature. All these conditions are interrelated and affect the conductivity. Because the physical properties of slag are unusual, special measurement techniques must be developed to insure adequate control over the measurement conditions.

A four probe dc measurement technique has been developed which eliminates or minimizes many of the difficulties usually encountered in slag conductivity measurements. The slag is held in a cylindrical crucible made of dense aluminum oxide. The electrodes are attached by a special process after the crucible is filled with the slag specimen to be studied. This approach eliminates the errors which usually ensue when an open boat is used, i.e., (a) slag surface oxidation or reduction effects, and (b) sample size and shape variation during the course of the measurement, particularly when going through a liquid-solid transition.

Careful measurements as a function of temperature and oxygen pressure are taken of voltages between all probe sets. Extensive measurements have been made on an Eastern slag from a Bow, NewHampshire, steam generating plant. This slag is typical of a high iron content slag where the conductivity originally was thought to be due in large part to a semi-conductive exchange of electrons between Fe^{+2} and Fe^{+3} ions in the slag. Present measurements indicate that at high temperatures (above 1385 °C) the conductivity is due primarily to the movement of iron ions while at low temperatures (below 1000 °C) the conductivity is probably due to a crystalline bridging in a noncrystalline matrix. The amount of crystalline material depends on the slag composition as well as the temperature and time from which it was cooled from the liquid to solid state. The conductivity above 1385 °C depends on the iron and not the potassium content or on the ambient oxygen pressure. Furthermore, at high temperatures the conductivity appears to be governed by the Walden Rule, i.e., $\sigma \cdot \eta$ = constant where σ is the conductivity and η is the viscosity since the conductivity more than doubles when the iron content is doubled. Iron additions lower the viscosity of the melt.

Other Activities of the
Ceramics, Glass, and Solid State Science Division

Invited Talks

Thermodynamics of Selected (K_2O, CaO)-rich Aluminosilicate Melts
82nd Annual Meeting of the American Ceramic Society,
Chicago, Illinois
L. P. Cook
April 30, 1980

Quasichemical Melt Polymerization Model of Seed/Slag Interaction
7th International Conference on Electrical Power Generation,
MIT, Cambridge, Massachusetts
L. P. Cook
June 16, 1980

Interfacially Controlled Phenomena in the System K_2CO_3-$KAlO_2$
Proceedings on Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems, Berkeley, California
L. P. Cook
July 29, 1980

High Temperature Melting Point Determinations at High Pressure
Department of the Army, Ballistic Missile Defense, Advanced
Technology Center, Huntsville, Alabama
G. J. Piermarini
October 1979

Analysis of Thermally Generated Microstresses in Polycrystalline
Beryllium Due to Beryllium Oxide Inclusions, 7th Intl. Symposium
on Thermal Expansion, ITT Research Institute, Chicago, Illinois
T. A. Hahn and R. W. Armstrong
November 1979

AB_4 Compounds
Gordon Research Conference
Santa Barbara, California
S. Block
January 1980

X-ray Diffraction of Single Crystals Under High Pressure
Crystallography at High Pressures (Workshop), Max Planck
Institute for Solid State Research, Stuttgart, West Germany
G. J. Piermarini
May 1980

X-ray Diffraction of Polycrystalline Materials Under High Pressure
Crystallography at High Pressures (Workshop), Max Planck Institute
for Solid State Research, Stuttgart, West Germany
G. J. Piermarini
May 1980

Low Temperature Studies with the Diamond Anvil Pressure Cell
Gordon Research Conference
Meriden, New Hampshire
R. G. Munro
June 1980

Computer Evaluation of Crystallographic Data
Denver X-ray Conference, Denver, Colorado
C. R. Hubbard, J. K. Stalick, and A. D. Mighell
August 1980

Computer Evaluation of Crystallographic Data
American Crystallographic Association Summer Meeting
University of Calgary, Calgary, Alberta, Canada
J. K. Stalick, A. D. Mighell, and C. R. Hubbard
August 1980

Restricted Diffusion of Biopolymer Molecules in Right Porous Matrices
Columbia University, New York, New York
W. K. Haller
November 28, 1979

Preparation and Properties of Fluorophosphate Glasses
Glass Through Chemical Processing, Rutgers University
New Brunswick, New Jersey
J. T. Wenzel, D. H. Blackburn, and W. K. Haller
March 20, 1980

Amorphous Thin Films by Codeposition
Glass Division Meeting, American Ceramic Society
Chicago, Illinois
D. M. Sanders, E. N. Farabaugh, and W. K. Haller
April 30, 1980

Sodium and Boron Vaporization from a Borosilicate Glass Melt
Glass Division Meeting, American Ceramic Society
Chicago, Illinois
J. T. Wenzel and D. M. Sanders
April 30, 1980

The Photoelastic Effect in Optical Materials
Topical Conference on Basic Optical Properties of Materials
National Bureau of Standards, Washington, D.C.
A. Feldman
May 7, 1980

Approaches to Eddy Current Inversion Problems
Workshop on Eddy Current NDE
General Electric Co., Schenectady, New York
A. H. Kahn
February 12, 1980

Technical and Professional Committee Participation and Leadership

American Ceramic Society
Committee on Publications of the American Ceramic Society
Subcommittee on "Phase Diagrams for Ceramists"
R. S. Roth, Chairman

American Society for Testing and Materials
C-8: Refractories
W. S. Brower, Member

C-21: Ceramic Whitewares and Related Products
H. S. Parker, Member

C. R. Robbins
Member: E-38: Resource Recovery
C-38.06.03 Fly Ash in Construction Materials
C-9: Concrete and Concrete Aggregates
C-18: Natural Building Stones
C18.0304: Sandstone

JCPDS-International Centre for Diffraction Data
C. R. Hubbard
Member: Technical Committee
Education Subcommittee
Computer Subcommittee
NBS Research Associate Advisory Subcommittee
Data Base (AIDS) Task Group
Chemical Informtion System Task Group

International Commission on Glass
W. K. Haller, U.S. Representative

International Commission on Glass
Subcommittee VIII, Standard Reference Glasses
W. K. Haller, Vice Chairman

International Commission on Glass
Subcommittee A, II-Durability and Analysis
W. K. Haller, Member

American Society for Testing and Materials

C-14 on Glass and Glass Products
M. J. Cellarosi, Vice Chairman
W. K. Haller, Member
D. J. Cronin, Member

C14.01: Nomenclature of Glass and Glass Products
M. J. Cellarosi, Chairman

C14.03: Chemical Properties of Glass
W. K. Haller, Member

C14.04: Physical and Mechanical Properties of Glas
M. J. Cellarosi, Member
D. J. Cronin, Member

C14.08: Flat Glass
M. J. Cellarosi, Member

American Society for Testing and Materials
M. J. Cellarosi
Member: E-38 Resource Recovery
E-44 Solar Heating and Cooling

American National Standards Institute
M. J. Cellarosi
Member: F-1 Hybrid Electronics

D. J. Cronin
Member: Z-26.1 Safety Glazing of Motor Vehicles
Z-97 Architectural Safety Glazing

Joint Electron Devices Engineering Councils
M. J. Cellarosi, Member

Electronic Industries Association
Committee on X-ray and Implosion TV Standards
M. J. Cellarosi, Member

Steering Committee, Greater Washington Solid State Physics Colloquium
M. I. Bell
Member 1979-1980, Treasurer 1980-1981

ASTM Committee F1, Subcommittee 2 on Lasers
A. Feldman, Editor

Advisory Board of the CRC Handbook Series in Laser Science and Technology
A. Feldman, Member

Review Panel for DOE MHD Contract at Montana State University
Bozeman, Montana, November 1979
W. R. Hosler, Member

Basic Microprocessor Course
M. I. Cohen (taught another session, Center-funded, Fall 1979)

Publications

Neutron Powder Diffraction Study of Ta_2WO_8
A. Santoro, R. S. Roth, and D. B. Minor
Acta Cryst., B35, 1202 (1979)

Magnetic Properties and Hyperfine Interactions in the b"' Phase of Potassium Ferrite
V. P. Romanov, G. A. Candela, R. S. Roth, and L. J. Swartzendruber
J. Appl. Phys., 50 [10] 6455 (1979)

Structure of (3-Chloro-2-hydroxy-5-nitrophenyl)-(2'-chlorophenyl) iodonium Hydroxide Inner Salt
S. W. Page, E. P. Mazzola, A. D. Mighell, V. L. Himes, and C. R. Hubbard
J. Am. Chem. Soc., 101, (1979)

The Synthesis and Crystal and Molecular Structure of $((C_7H_7)_3P_4Cu_4W_2S_4)$, a Dimer of Bis((tri-p-tolylphosphine)copper) oxotrithiotungsten
R. M. Doherty, C. R. Hubbard, A. D. Mighell, A. R. Siedle, and J. M. Stewart
Inorg. Chem. 18, 2991 (1979)

ADOBE II: Factors Affecting the Durability of Adobe Structures
P. W. Brown, C. R. Robbins, and J. R. Clifton
Studies in Conservation 24, 23 (1979)

Influence of P_{O_2} on Vaporization of Odium Disilicate at 1345 °C
D. M. Sanders and W. K. Haller
J. Amer. Ceram. Soc., 62 424 (1979)

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A. Feldman, R. M. Waxler, and I. H. Malitson
SPIE Proc., Vol. 204, Physical Properties of Optical Materials, pp. 95 (1979)

Properties of Crystalline Materials for Optics
A. Feldman and R. M. Waxler
SPIE Proc., Vol. 204, Physical Properties of Optical Materials, pp. 68 (1979)

Eddy Currents in a Conducting Cylinder with a Crack
R. Spal and A. H. Kahn
J. Appl. Phys., 50, 6135 (1979)

MHD Materials
S. J. Schneider, T. Negas, and H. P. R. Frederikse
Rev. Int. des Hautes Temp. Refract., Fr. 16, 169 (1979)

Interfacially Controlled Phenomena in the System K_2CO_3-$KAlO_2$
L. P. Cook
Proceedings on Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems, Berkeley, California (July 1980)

A Preliminary Industrial Evaluation of the Fluidic Capillary Pyrometer
R. M. Phillippi and T. Negas
Proceedings of ASME 20th Annual Conference on Fluidics, Chicago, Illinois
(November 1980)

Fluidic Capillar Temperature Sensors: Materials, Design, and Fabrication
T. Negas, H. S. Parker, W. S. Brower, R. M. Phillippi,
T. M. Drzewiecki, and L. P. Domingues
Proceedings of ASME 20th Annual Conference on Fluidics, Chicago, Illinois
(November 1980)

Phase Equilibria Research in Portions of the System K_2O-MgO-Fe_2O_3-Al_2O_3-SiO_2
R. S. Roth
Advances in Chemistry Series #186, Solid State Chemistry: A Contemporary Overview (November 1980)

Platinum Thiotungsten Compounds. Crystal and Molecular Structure of Bis(Triethylphosphine)platinum Tetrathiotungsten
A. R. Siedle, C. R. Hubbard, A. D. Mighell, R. M. Doherty, and
J. M. Stewart
Inorg. Chem. Acta 38, 197 (1980)

New Bond-Delocalized Dianions: The Crystal Structure of 1:3-Bis (dicyanomethylene) Cronconate Salt
V. L. Himes, A. D. Mighell, C. R. Hubbard, and A. J. Fatiadi
J. Res. NBS, 85, No. 2, March-April 1980

Synthesis and Antitumor Activity of Cyclophosphamide Analogs.
3. Preparation, Molecular Structure Determination, and Anticancer Screening of Racemir cis- and trans-Phenylcyclophosphamide
V. L. Boyd, G. Zon, V. L. Himes, J. K. Stalick, A. D. Mighell,
and H. V. Secto
J. Med. Chem. 23, 372 (1980)

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C. R. Hubbard, A. D. Mighell, and A. J. Fatiadi
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A. D. Mighell and J. R. Rodgers
Acta Cryst. A36, 321 (1980)

The Reliability of Powder Indexing Procedures
A. D. Mighell and J. K. Stalick
Proc. of Accuracy in Powder Diffraction, NBS Spec. Pub. 567
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Standards for the Publication of Powder Patterns: The American Crystallographic Associations Subcommittee Final Report
L. D. Calvert, J. L. Flippen-Anderson, C. R. Hubbard, Q. C. Johnson, P. G. Lenhert, M. C. Nichols, W. Parrish, D. K. Smith, R. L. Snyder, and R. A. Young
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February 1980

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C. R. Hubbard
Proc. Accuracy in Powder Diffraction Symposium, NBS Spec. Pub. 567
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R. G. Munro
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R. G. Munro, S. Block, and G. J. Piermarini
La Recherche 113, 806 (1980)

Analysis of Thermally Generated Microstresses in Polycrystalline Be Due to the Presence of BeO Inclusions
T. A. Hahn
Proc. Thermal Expansion Symposium, 1980

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James Mattie, Charles H. Berg, and Mario Cellarosi
in "Materials Aspects of World Energy Needs," pp. 151-154
National Research Council, National Academy of Sciences, 1980

Dielectric, Pyroelectric, and Thermal Properties of $LiNH_4SO_4$ and $LiND_4SO_4$
G. M. Loiacono, M. Delfino, W. A. Smith, M. I. Bell, A. Shaulov, and Y. H. Tsuo
Ferroelectrics 23, 89 (1980)

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M. Delfino, G. M. Loiacono, W. A. Smith, A. Shaulov, Y.H. Tsuo, and M. I. Bell
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Improper Ferroelectrics for Pyroelectric Detection of Infrared Radiation
A. Shaulov, W. A. Smith, G. A. Loiacono, M. I. Bell, and Y. H. Tsuo
Ferroelectrics, 27, 117 (1980)

Electroreflectance of PZT Ceramics
S. H. Shin, F. H. Pollak, and M. I. Bell
Ferroelectrics, 27, 147 (1980)

Strain-Induced Splitting and Oscillator Strength Anisotropy in Calcium Fluoride, Strontium Fluoride, and Barium Fluoride
A. Feldman and R. M. Waxler
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A. Feldman and R. M. Waxler
Basic Optical Properties of Materials Summaries of Papers, ed. A. Feldman, NBS Spec. Pub. 574 (USGPO, Washington: 1980), pp. 204

Radiation Damage in $MgAl_2O_4$
G. P. Summers, G. S. White, K. H. Lee, and J. H. Crawford, Jr.
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G. S. White, K. H. Lee, and J. H. Crawford, Jr.
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Electrical Conductivity Mechanisms in Iron Containing Slags
W. R. Hosler, G. S. White, and T. Negas
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Quasichemical Melt Polymerization Model of Seed/Slag Interaction
L. P. Cook
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Cambridge, Massachusetts (June 1980)

Materials for Open Cycle MHD Generators
S. J. Schneider, H. P. R. Frederikse, T. Negas, and G. Rudins
in Current Topics in Materials Science, Vol. 4, North Holland Publishing Co., 1980

Neutron Powder Diffraction Study of the Structures of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$
A. Santoro, M. Marezio, R. S. Roth, and D. B. Minor
J. Solid State Chemistry (in press)

Thermal Stability of Long-range Order in Oxides
R. S. Roth
Progress in Solid State Chemistry (in press)

The Structure of $LaTaO_4$ at 300 °C by Neutron Powder Profile Analysis
R. J. Cava and R. S. Roth
J. Solid State Chemistry (in press)

Ternary Compounds in the $BaO-Nd_2O_3TiO_2$ System
D. Kolar, S. Gaberscek, B. Volavsek, H. S. Parker, and R. S. Roth
J. Solid State Chemistry (submitted)

(3-Chloro-2-oxo-5-nitrophenyl)(2-chlorophenyl) Iodonium, Inner Salt
C. R. Hubbard, V. L. Himes, A. D. Mighell, and S. W. Page
Acta Cryst. (in press)

Registration/Identification of Crystalline Materials Based on Lattice and Empirical Formula
J. R. Rodgers and A. D. Mighell
J. Chem. Inf. Comp. Sci. (in press)

Determination of the Relationship Between Derivation Lattices
A. Santoro, A. D. Mighell, and J. R. Rodgers
Acta Cryst. (in press)

High Pressure Crystallography (invited paper)
S. Block and G. J. Piermarini
in "History of Crystallography" (submitted to WERB July 1980)
to be published by Am. Cryst. Assn.

Viscosity and Glass Transitions in Liquids at High Pressures (invited paper)
R. G. Munro, G. J. Piermarini, and S. Block
(submitted to WERB)(to be published in J. Phys. Chem. Japan)

Vaporization in an Unstirred Soda-Lime-Silica Glass Melt
S. Murai, J. T. Wenzel, and D. M. Sanders
Phys. Chem. Glasses (accepted)

The Effect of Striae on the Strength of Glass
W. Capps, H. Schaeffer, and D. J. Cronin
J. Amer. Ceram. Soc. (accepted)

The Role of Water Vapor and Sulfur Compounds on Sodium Vaporization During Glass Melting
D. M. Sanders, M. E. Wilke, S. A. Hurwitz, and W. K. Haller
J. Amer. Ceram. Soc. (submitted)

A Standard Technique for Measuring Window Absorption and Other Efficiency Losses in Semiconductor Energy Dispersive X-ray Spectrometry
R. E. Stone, F. J. Walter, D. H. Blackburn, P. Pella and H. Kraner
J. X-ray Spectrometry (submitted)

Viscosity-Temperature Relationships at One Atmosphere in the System Diopside-Anorthite
C. M. Scarfe, D. J. Cronin, J. T. Wenzel, and D. A. Kauffman
1979-1980 Yearbook of the Carnegie Institute, Washington, DC
(submitted to WERB)

Effects of Inhomogeneous Strain in Ferroelectric Crystals Near Their Phase Transitions
G. M. Loiacono, M. Delfino, A. Shaulov, W. A. Smith, and M. I. Bell
Ferroelectrics (to be published)

Complications in the Use of Raman Spectroscopy to Diagnose Annealing of Boron-Implanted Silicon
R. A. Forman, M. I. Bell, and D. R. Myers
J. Appl. Phys. (to be submitted)

Effects of Stress on the Raman-Active Modes in Semiconductors
M. I. Bell
Proc. VIIth Int. Conf. on Raman Spectroscopy (to be published)

Electro-oxidation of Hydrogen in Mo-W Carbide Alloy Catalysts in Acid Electrolyte
A. J. McAlister and M. I. Cohen
Electrochimica Acta (submitted)

A Boundary Integral Equation Method for Calculating the Eddy Current Distribution in a Long Cylindrical Bar with a Crack
A. H. Kahn and R. Spal
Proc. Symposium on Eddy Current Characterization
(accepted for publication by ASTM)

Disappearance of Impurity Levels in Silicon and Germanium Due to Screening
J. R. Lowney, A. H. Kahn, J. L. Lue, and C. L. Wilson
J. Appl. Phys. (submitted)

The National Bureau of Standards Optical Measurement Program
Refractive Index, Thermo-optic Constants and Photoelastic Constants
A. Feldman, M. J. Dodge, D. Horowitz, and R. M. Waxler
Tenth Anniversary Volume, Laser Damage Symposia (accepted)

Temperature Dependence in Air of Fe^{2+} Concentration in a Natural Eastern Coal Slag
G. S. White, W. R. Hosler, and T. J. Castellano
J. Am. Ceram. Soc. (submitted)

Chemical Degradation of Castable Refractories in Coal Gasification Process Environments
C. R. Robbins and F. A. Mauer
J. Materials for Energy Systems (in press)

Strength, Erosion, and Phase Equilibrium of Refractory Concretes in Coal Gasification Environments
S. M. Wiederhorn, E. R. Fuller, Jr., and C. R. Robbins
in <u>Properties and Performance of Materials in Coal Gasification Environment</u>, ASM (in press)

Lead Alkali Apatites Without Hexad Anion: The Crystal Structure of $Pb_8K_2(PO_4)_6$
M. Mathew, W. E. Brown, M. A. Austin, and T. Negas
J. Solid State Chemistry (in press)

Piezo-optic Coefficients of Four Neodymium-doped Laser Glasses
R. M. Waxler and A. Feldman
Appl. Opt. (accepted)

Division Seminars

Dr. Joseph Shamir, Israel Institute of Technology
"Determination of the Optical Constants of a Thin Film"
September 21, 1979

Professor Joel Bernstein, Ben-Gurion University
"Influence of Crystal Forces on Molecular Conformation"
October 18, 1979

Professor Philip Coppens, SUNY, Buffalo
"Experimental Charge Densities in Inorganic Materials"
November 13, 1979

Dr. Tom Soules, General Electric Company
"A Molecular Dynamics Calculation of the Structure of Sodium Silicate Glasses"
January 8, 1980

Dr. Sally H. Hunter, Florida International University
"EXAFS Structural Studies of Compound Amorphous Demiconductors"
February 1, 1980

Dr. Ulrich Strom, Naval Research Laboratory
"Spectroscopy of Tunneling Modes in β-Alumina Fast Ion Conductors"
February 5, 1980

*Dr. Joe Wong, G.E. Corporate Research and Development
"EXAFS Studies of Glassy Solids"
March 4, 1980

Dr. Marcel Pulain, Universite de Rennes
"Zirconium Fluoride Glasses"
March 24, 1980

Dr. Albert Wright, Institut Lane-Lanjevin, France
"Observations of Nucleation in Glass-Ceramics by SANS"
May 16, 1980

*Joint with Center for Materials Science

Dr. R. S. Roth, CMS (NBS)
"Use of High Resolution Electron Microscopy in Ceramic Research"
June 11, 1980

Professor Robert Snyder, Alfred University
"Rebirth of X-ray Powder Diffraction"
August 1, 1980

External Recognition

IR 100 Award for development of low non-linear refractive index laser glass
September 1979

Books

Phase Diagrams for Ceramists
Edited by L. P. Cook, R. S. Roth, T. Negas, and G. W. Cleek
Published by the American Ceramic Society, Columbus, Ohio
Volume 4 (in press)

Accuracy in Powder Diffraction. Proceedings of Accuracy in Powder Diffraction Symposium, June 1979
S. Block and C. R. Hubbard, eds.
NBS Special Publication 567, 571 pp., February 1980

PDF Workbook: Use of X-ray Powder Diffraction File
C. R. Hubbard, G. McCarthy, and C. Foris
(To be published by the JCPDS--International Centre for Diffraction Data)(in press)

Basic Optical Properties on Materials--Summaries of Papers, May 1980
A. Feldman, ed.
NBS Special Publication 574, 241 pp., 1980

Special Reports

Slag Characterization: Viscosity of Synthetic Coal Slag in Stem
W. S. Brower, J. L. Waring, and D. H. Blackburn
NBSIR Report, prepared for DOE, June 1980

A High Temperature Transpiration Apparatus for the Study of the Atmosphere Above Viscous, Incongruently Vaporizing Melts
D. M. Sanders and W. K. Haller
Proceedings of the Tenth Materials Research Symposium on Characterization of High Temperature Vapors and Gases
National Bureau of Standards, Gaithersburg, Maryland, September 18-22, 1978
NBS Special Publication 561, Vols. I and II (1979)

AUTO, A Real Time Diffractometer Control System for the Interdata 7/16 Computer
R. L. Snyder, C. R. Hubbard, and N. C. Panagiotopoulos

Chemical Degradation of Castable Refractories in Coal Gasification Process Environments
C. R. Robbins and F. A. Mauer
NBSIR 80-2064, Final Report to the U.S. Department of Energy, May 1980

Measuring the Rate of Corrosion of Reinforcing Steel in Concrete
E. Escalante, S. Ito, and M. I. Cohen
NBSIR 80-2012, For the Federal Highway Administration, March 1980

"User Evaluation of Crystal Data Products and Services: Questionnaire Analysis and Impact"
NBS Tech. Note 1112, June 1980
J. K. Stalick, A. D. Mighell, and R. J. Boreni

Materials for Fuel Cells
L. H. Bennett, M. I. Cohen, A. L. Dragoo, A. D. Franklin, and A. J. McAlister
NBS number not assigned, for DOE period covered January-December 1979, in press

Quarterly Reports to DOE of NBS Contract work on Conductivity Mechanisms in Coal Slag
W. R. Hosler

<u>Standard Reference Materials</u>

SRM 733 Certified--Gradient Furnace Liquidus Standard

<u>Patents</u>

Hybrid Temperature-Oxygen Fugacity Sensor
T. Negas, L. P. Domingues, T. Drzewiecki, and R. M. Phillippi
March 1979 (pending)

<u>Sponsored Conferences</u>

NML Topical Conference on Basic Optical Properties for Materials, NBS/OSA, Gaithersburg, Maryland, May 5-7, 1980
A. Feldman, Chairman, Organizing and Program Committee

REACTOR RADIATION DIVISION (566)

Robert S. Carter, Chief
Tawfik M. Raby, Deputy Chief
E. C. Maxwell, Administrative Officer
L. L. Sprecher, Secretary
T. L. Mangum, Secretary

The Reactor Radiation Division (RRD) has the dual functions of operating the NBS Reactor (NBSR) and using neutron scattering methods for the study of materials. The first function includes not only the operation of the reactor, but also providing sample irradiation services for a large number of users. The second function includes, in addition to Division materials research programs, serving as a focal point of neutron scattering expertise for many other programs within and without the Bureau.

A major part of the overall Reactor Division contribution to the NBS mission and to the scientific and technical community is in fostering the utilization of the reactor by other NBS groups and outside organizations. Interactions with other scientists and organizations take the form of both collaborative efforts and independent programs which rely on utilization of the reactor and facilities provided by the NBSR staff. The extent of such interactions for FY80 are indicated in the tables below. The number of personnel shown in tables 1 and 2 include many short-term collaborators as well as permanent other agency and university guest workers. These numbers are constantly changing and so may not be exact.

Collaborative interactions are those in which workers from outside the RRD collaborate scientifically with RRD scientists on problems of mutual interest. These interactions are summarized in table 1.

Table 1. Collaborative Interactions

	No. of Personnel FY 80
RRD Permanent Scientists	12
Non-RRD Participants	
Other NBS	21
Other Agency	39
University	30
Industrial	10
Total Non-RRD	100

Independent programs are those programs carried out independently of the Reactor Radiation Division scientific staff by other NBS Divisions and outside organizations. Table 2 summarizes these interactions.

Table 2. Independent Programs

	No. of Personnel FY 80
Other NBS	35
Other Agencies	20
Universities	18
Total	73

These tables demonstrate the extensive utilization of the NBS reactor by scientists and engineers from outside the Division. They come from 18 NBS Divisions and offices, 18 Federal agencies, and national laboratories, and more than 25 universities and industrial laboratories.

Many of the other agency and university collaborators have worked with us regularly for many years. Five of them (two from the Navy and three from the Army) are assigned to work full time at the reactor on a permanent basis. Others regularly spend two or three days a week at the reactor. Bureau collaborative programs include measurements on ionic crystals, polymers, simple liquids, surface molecules, hydrogen embrittlement, etc. Major independent (non-collaborative) Bureau programs include trace analysis by a neutron activation analysis, standard neutron fields for neutron flux calibration and materials dosimetry, and precision gamma-ray energy measurement.

Many outside organizations use the sample irradiation services offered by the Division. Major users include the FBI, FDA, U.S. Geological Survey, the Smithsonian Institute, and the University of Maryland. Programs range from analysis of criminal artifacts to the measurement of pollutants in the environment.

The reactor modernization is nearing completion. The cooling tower basin should be completed in September and the new cooling tower installed shortly thereafter. The completion of the secondary piping modifications will be completed in the fall.

The Safety Analysis Report in support of our application for a 20 MW license has been completed and the additional supporting information required to renew our operating license for another 20 years is being prepared. Because public hearings are anticipated, the licensing process is anticipated to take at least a year from date of submittal of the application.

The new fuel elements from our new supplier, Texas Instruments, are starting to be delivered and the total order which should last until about the end of calendar year 1982 should be delivered within the next year. Unfortunately, once again the fuel element manufacturer has succumbed to the ever-growing web of NRC regulation and will go out of the fuel element business as soon as their present commitments are met. They are also suppliers for all the large DOE research reactors and so we are joining with DOE in an attempt to establish a new vendor.

The mechanical problem with the reactor shim arms, reported last year, has been repaired. All the shim arms and most of the other parts (bearings, etc.) had to be replaced. The manufacture of replacement parts and the very complex work of replacement caused a shutdown of almost seven months. This, of course, severely reduced the reactor utilization and many users of our irradiation services had to go elsewhere temporarily. The beam hole users had no equivalent place to go and so were particularly hurt. The reactor was put back on line in February 1980 and has been operating smoothly ever since.

The large number of independent programs (those that do not involve scientific collaboration) were curtailed somewhat because of the reactor shutdown. Nevertheless, a great deal was accomplished and is described in the "Summary of Activities, July 1979-June 1980," (Preliminary copies can be made available to interested groups. These programs include the characterization of standard reference materials, environmental pollutants, food and drugs, criminal artifacts, solar cell materials, etc., through the use of neutron activation analysis to determine the level of trace elements. The Center for Radiation Research continues to develop neutron field measurement systems and to provide filtered beams for neutron dosimetry calibration and development. New methods of analysis are being developed such as neutron methods for determining the concentration of trace elements as a function of depth from the surface (depth profiling). Renewed interest has been expressed by NIH in the production of fluorine-18 for use in brain research. The Quantum Metrology Group continues to extend their work in the absolute measurement of γ-ray wavelength and the joint NBS-University of Maryland program in prompt γ-ray trace analysis continues to expand its area of applicability.

The scientific work of the Reactor Radiation Division and its collaborators are summarized later in this report and details are given in the "Summary of Activities" mentioned earlier. A few highlights will be given here to indicate the current direction and accomplishments of the Division.

During the past year there has been considerable research and instrumentation development associated with our Division's competence initiative in advanced neutron methods. Detailed design of the state-of-the art NBS small angle scattering facility has been completed, major construction items have been completed or are under construction, the first (25 x 25 cm) area detector has been tested successfully, and a major fraction of the data acquisition network, data analysis software, and graphics system has been completed. SANS cooperative research activities have been initiated with the Navy labs, SUNY, and the NBS Metallurgy Division on metallurgical applications, and with the industrial labs and the University of Illinois on studies of magnetic correlations in spin glasses and amorphous magnets. A second full-time staff member has been hired and two IPA Fellows have been brought in to enhance research activities on polymers and alloy microstructure.

Other significant developments include the completion of a new, high-intensity neutron analyzer and its successful application in the first neutron study of a chemisorbed hydrocarbon monolayer on an industrial catalyst. We have also achieved the first observation of the interaction of tunneling molecular impurities in with phonons in a solid. Neutron studies have been initiated on structure, critical behavior, and spin interactions in a new class of amorphous alloys showing a transition from ferromagnetic order at high temperature to spin glass behavior at lower temperatures. In our neutron diffraction and radiography task, we have continued our efforts to advance powder diffraction and profile refinement techniques by introducing improved lineshape analysis methods and evaluation of these techniques for determining magnetic moments in multisublattice compounds. There has been a further expansion of our applications of high-resolution neutron diffraction to high-technology materials, involving, e.g., new cooperative research efforts with industrial guest workers. In our radiographic standards and NDE projects we have completed a cooperative project with private labs using radiographic reference methods to nondestructively observe chemical mobility associated with the rundown of cardiac pacemakers and determined the optimum ratio of $^{6}Li/ZnS$ for use in high-speed imaging systems.

During the coming year we, of course, anticipate final testing and operation of the NBS SANS Facility and an associated increase in cooperative measurement, research, and NDE activities, most specifically in the area of polymer science, advanced magnetic materials, and in the studies related to durability, performance, and processing of metals and alloys. Our Division will also be engaged in the development of neutron irradiation and materials characterization techniques for use in the new NBS program on nuclear waste. Expanded research is also anticipated in the study of chemical processes on catalytic surfaces and on new applications of neutron scattering methods for atomic scale studies of hydrogen in defected and corroded alloys.

The Division's activities are organized into four primary tasks:

12161	REACTOR OPERATION AND SERVICES
12162	NEUTRON SCATTERING CHARACTERIZATION OF MATERIALS FOR ADVANCED TECHNOLOGIES
12163	NEUTRON DIFFRACTION AND RADIOGRAPHIC METHODS FOR MATERIALS UTILITY AND DURABILITY
51102	ADVANCED NEUTRON METHODS

The following sections describe these in more detail.

REACTOR OPERATIONS AND SERVICES
Task 12161

Shortly after the beginning of this reporting year, a mechanical problem which developed with one of the shim arms forced an extended reactor shutdown of nearly seven months. The problem was finally traced to a swelling of the cadmium blade which necessitated replacement of all four blades. The replacement process which had never been done before proved to be both difficult and complex because everything had to be done remotely due to the highly radioactive components and environment involved. In addition, a great deal of preparation had to be made including preparation of methods and procedures, design and construction of heavy shield cask, design and fabrication of tools and equipment, and fabrication of critical replacement parts.

The old shim arms were the original installed in the reactor during construction more than 12 years before. They had already lasted significantly longer than expected due to a very effective fuel management program. The blades had approximately two more years lifetime and were scheduled for replacement in 1981 during the conversion to 20 MW. The shim arm replacement operations were performed entirely in-house. They were carried out smoothly and efficiently and with absolute safety. There was little or no exposure to personnel.

During this period several other major tasks were undertaken. They included inspection of the reactor internal piping and overhaul of the fuel transfer system. A new fuel element design was installed in the reactor that will provide even greater fuel utilization efficiency, already one of the best in the country. Significant progress was made toward reactor modernization including procurement of a new cooling tower and design of all new or modified systems.

The reactor returned to routine operation at the end of February. The last four months saw probably the heaviest utilization in its history. At present, 18 NBS Divisions and offices, 18 other Government agencies and national laboratories, and 15 universities and industrial labs involving more than 200 scientists and engineers use more than 23 simultaneously operable reactor facilities. This is probably the widest and most diversified use of any reactor in the U.S.

Reactor Operations
Subtask 1 of Task 12161

T. M. Raby, J. F. Torrence

Reactor operating schedule was curtailed last year due to the replacement of the shim arms. Most of the effort of operations and engineering personnel was directed toward returning the reactor to normal as quickly as possible. A summary of overall statistics is presented in the following table for the period July 1, 1979 to June 30, 1980.

NBSR OPERATING SUMMARY FY 80

Number of days at 10 MW	122
On-line time at 10 MW	33%
Average U-235 burnup	50%
Number of Irradiations	1160
Hours of Irradiations	1600
Hours per Irradiation	1.4

Irradiation Services
Subtask 2 of Task 12161

N. A. Bickford, J. H. Ring

During the short period the reactor operated last year there was perhaps the heaviest use of irradiation facilities in the history of the reactor. Activation Analysis continued on a large scale. Among these are analyses of foods, drugs, environmental samples, forensic investigation, development of energy resources and raw materials, and the production of important standard reference materials.

Among new programs that have been initiated are the establishment of a National Environmental Sample Bank and ultraprecise analysis of atmospheric samples from all over the world. Discussions are also underway with NIH, the National Naval Medical Center, and Johns Hopkins for the production of fluorine-18 in a pioneering program for direct study of functions of vital organs and human cells.

Engineering Services
Subtask 3 of Task 12161

J. H. Nicklas, R. S. Conway

Aside from the engineering support provided to reactor operations and experimenters, engineering services were heavily involved in three major areas. These are the successful resolution of the shim arm problem and subsequent replacement, reactor modernization, and procurement and inspection of new fuel elements for future reactor use.

The shim arm problem was probably one of the most demanding ever encountered in the operating history of the NBSR. Extensive engineering, design, fabrication, machining, and procurement were required. Engineering services personnel were also involved in several aspects of the actual replacement and installation of components, all performed remotely underwater. The careful planning and conduct of all operations resulted in the smooth and efficient reassembly and reinsertion of the new assemblies into the reactor. These were perhaps the most crucial and potentially damaging operations of the entire project.

Production of the new fuel element design was started this year and the first batch of elements were inspected, accepted, and delivered in time for use in the reactor.

Significant progress was made toward the reactor modernization. The new cooling tower design was completed and a contract was awarded for construction in the summer of 1980. Similarly the cooling tower basin design was finalized and construction has already started. Design of the extensive secondary piping, relocation of pumps, and a new chemical treatment center were also completed. A portion of the new secondary system is already in place with the balance to be completed once the new cooling tower is installed. All electrical connections design and specifications were also finalized. A comprehensive design plan of new nuclear, process, and monitoring instrumentation has been prepared. Most of the components and equipment have been specified and obtained. These will be assembled, tested, and installed periodically whenever reactor shutdown permits.

NEUTRON SCATTERING CHARACTERIZATION OF MATERIALS FOR ADVANCED TECHNOLOGIES
Task 12162

This task develops and applies advanced neutron scattering methods and related theoretical analysis for research on the microscopic properties of materials which affect their use in technological applications. Current areas of emphasis include hydrogen in metals, new magnetic and glassy materials, and molecular solids. The neutron inelastic, quasi-elastic, and magnetic scattering techniques applied provide unique information, e.g., on phase transformations, interatom bonds, electronic structure, sublattice magnetization, hydrogen binding and diffusion, and molecular and crystal dynamics. The members of this task (and the following task) are also responsible for establishing and maintaining a center of excellence for neutron scattering and radiographic measurements including a computer-controlled network of 11 spectrometers at the reactor. Task scientists couple directly with other NBS and outside groups who require state-of-the art neutron measurement methods and expertise in their programs. Examples include long-term collaborative efforts with in-house guest workers from Army Materials, Naval Research Laboratory, Naval Surface Weapons Center, and the University of Maryland on materials for improved microwave transmission and sonar and advanced explosive formulations; cooperative research with industrial scientists (Allied Chem., G.E., IBM) on new classes of materials with potential applications for advanced power transformers, computers, and energy storage; and research on hydrogen in metals and prototype phase transformations in solids with other national laboratories (Argonne National Laboratory, Brookhaven National Laboratory) and universities (University of Illinois, University of Houston, University of Saarlande, University of Munich). In addition, staff scientists are actively engaged with other Divisions and Centers at NBS in the application of neutron scattering methods for: (1) surface analysis of chemical products and reactions on industrial catalysts; (2) ultrasensitive microscopic analysis of hydrogen in metals; and (3) corrosion in aluminum alloys.

Plans for the coming year include: (1) expansion of our measurements of the atomic scale behavior of low level concentrations of hydrogen in metals and alloys, including isotope effects and the study of tunneling states of impurity-trapped hydrogen; (2) initiation of a systematic study of the structure and magnetic properties of new transition-metal-metalloid glasses; and (3) exploration with the Chemical Stability and Corrosion Division of the application of neutron techniques to the study of stress corrosion products in alloys.

Microscopic Properties of Hydrogen in Metals and Molecular Materials
Subtask 1 of 12162

J. M. Rowe, J. J. Rush, S. F. Trevino[1], A. Magerl[2]

[1]Guest Worker, AMRAD
[2]Guest Worker, University of Munich

Examples of activities and accomplishments during the past year:

- Completed construction, installation, and testing of a new high-intensity filter-analyzer for highly sensitive neutron scattering investigations of hydrogen in metals and molecular reactions products on catalytic surfaces.

- Completed first measurements of hydrogen dynamics in the presence of interstitial and substitutional traps in refractory metals.

- Studied the chemisorption of ethylene on Raney nickel as a function of temperature using neutron vibrational analysis and initiated a test of neutron scattering for *in situ* determination of impurity levels on industrial catalysts.

- Completed first direct measurement of the interaction of tunneling levels of molecular impurities with phonons in an inorganic crystal $(KBr(CN^{-})_{0\,0003})$.

- Completed computer simulation of the crystal dynamics of β-phase NbD_x to explain the character of anomalous, low-energy hydrogen modes in this system.

- Achieved molecular dynamic simulation of an order-disorder transformation in a diatomic molecular crystal as part of an effort to investigate the mechanisms of redistribution of chemical reaction energies in condensed matter.

- Set up tripartite research program with scientists from Belgium and West Germany, partly supported by NATO, for expanded fundamental research on single particle dynamics and phase transitions in metal-hydrogen systems.

Microscopic Properties of Magnetic and Amorphous Materials
Subtask 2 of Task 12162

J. J. Rhyne, R. C. Casella, J. Lynn[1], H. Alperin[2] N. Koon[3], K. Hardman

[1]Guest Worker, University of Maryland
[2]Guest Worker, Naval Surface Weapons Center
[3]Guest Worker, Naval Research Laboratory

Examples of activities and accomplishments during the past year:

o Initiated neutron studies of a new class of amorphous alloys which show ferromagnetic order at higher temperature and spin glass behavior at low temperature, including an examination of both the critical properties and the spin dynamics through the transition from ferromagnetic to spin glass order.

o Completed detailed structure study of several hydrides of Th_6Mn_{23} and Y_6Mn_{23} to investigate the unique changes in magnetic properties of these compounds on hydrogenation.

o Initiated evaluation of the use of neutron profile refinement techniques in determining magnetic moments in multisublattice magnetic compounds.

o Developed a Greens function random phase approximation (RPA) computer model including both exchange and crystal field contributions and applied it to explain the anomalous finite temperature excitations of $ErFe_2$ and $ErCo_2$ and the ground state spin waves in $HoCo_2$.

o Expanded measurements of the crystal fields and magnetic order in a number of compounds which show coexistent phenomena of superconductivity and magnetism.

o Completed a study of spin waves in Rb $MnCl_3$, a ferromagnet with alternating strong and weak exchange couplings, and used a linear spin wave model used to analyze the results.

o The subtask leader was a member of a nine-member delegation from the U.S. invited to India to participate in a binational conference on rare earth materials.

NEUTRON DIFFRACTION AND RADIOGRAPHIC METHODS FOR MATERIALS UTILIZATION AND DURABILITY
Task 12163

This task utilizes the unique role of neutrons (due, e.g., to their deep penetration, sensitivity to light atoms, and well-defined lineshapes for precise structure analysis) in the structural analysis and non-destructive testing of materials. Task members have competences at the forefront of measurement and analysis of materials structure, including concentrated efforts in neutron powder diffraction and profile analysis methods, broad expertise in radiographic measurement technology, and state-of-the art computer controlled diffraction facilities. This expertise is used to develop advanced neutron diffraction and radiographic methods to provide: (1) precise structure analysis essential for effective use of materials (e.g., in batteries and chemical catalysis); (2) nondestructive reference methods for defects, precipations, and texture affecting metal product performance, for improved quality assurance, e.g., in pacemaker batteries, composites, and nuclear waste containment, and for microstructure analysis of materials in extreme environments; and (3) neutron radiography and beam standards for more accurate and reliable plant and field inspections (e.g., corrosion in aircraft). Current research and measurement activities include cooperative projects with the Center for Radiation Research (NDE), Center for Thermodynamics and Surface Science (properties of fluids and surfaces), and with four CMS Divisions (materials structure and durability). This task also directly serves the Offices of Nondestructive Evaluation and Nuclear Safeguards. Outside interactions and cooperative research with groups needing advanced neutron methods include NIH, NRL, Army Materials, Navy, FDA, aviation industries, Smithsonian, Allied Chemical Co., Bell Labs, Army, and universities on projects ranging from corrosion detection to the structure of proteins.

Plans for the coming year include: (1) installation, testing, and operation of the NBS small angle scattering spectrometer; (2) development with other CMS Divisions of expanded neutron diffraction and SANS applications in alloy solidification processes and durability, and in microstructure analysis of nuclear wasteforms; and (3) further work on improved methods for measuring and interpreting modulated structures in inorganic materials.

Neutron Diffraction Methods and Applications
Subtask 1 of Task 12163

E. Prince, A. Santoro, B. Mozer, H. Prask[1], C. Choi[1], A. Wlodawer

[1]Guest Worker, AMRAD

Examples of activities and accomplishments during the past year:

- Established cooperative research efforts with Bell Labs and Metronic, Inc., on the application of high-resolution neutron diffraction to provide critical structure information on prototype Li compounds for electronic applications.

- In our continuing efforts to advance powder diffraction and neutron profile refinement methods, we have introduced generalized variable lineshape refinement procedures to provide more reliable structural analysis in many cases where strain and particle size effects provide non-Gaussian diffraction profiles.

- Completed the first neutron diffraction data set on the enzyme ribonuclease using the NBS-NIH flat-cone diffractometer and utilized improved x-ray and neutron data reduction and refinement procedures to establish the configuration of the histadine side-chain critical to understanding the biochemical activity of this enzyme.

- Completed structure refinements of model metal-oxide compounds and ceramics as part of a continuing study of the microscopic properties of electronic ceramics and storage battery materials in cooperation with the Ceramics, Glass, and Solid State Science Division and NRL.

- Used neutron diffraction to determine atomic arrangements and particle sizes in graphite-intercalation compounds.

<u>Radiographic Methods and Standards</u>
Subtask 2 of Task 12163

D. A. Garrett, Y. T. Cheng, M. Ganozcy, W. L. Parker[1]

[1]Guest Scientist

Examples of activities and accomplishments during the past year:

- Completed the cardiac pacemaker study using neutron and x-ray power system techniques to explain the chemical kinetics of the battery components as a function of rundown. This work was performed in cooperation with engineers in the private sector.

- Completed the study of the validity of results obtained utilizing the Aerotest Operations method of measuring the L/D ratio parameter for neutron radiographic facilities.

- Completed a study to determine the feasibility of utilizing nuclear reactors in the Washington, D.C., area for the attribution and authentication of valuable paintings. This technique utilized the neutron-induced autoradiography method for the painting characterization.

- Completed the editing of the ASTM Special Publication, "Proceedings of the NBS Symposium on Real-Time Radiologic Imaging: Medical and Industrial Applications."

- Completed the evaluation of non-reactor based neutron radiography facilities for the Department of the Navy.

- Developed a mathematical procedure to address the matrix problems associated with nuclear waste quantification.

- Determined the optimum ratio of $^6Li/ZnS$ for use in high-speed neutron imaging systems.

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ADVANCED NEUTRON METHODS
Task 51102

C. Glinka, N. Berk, J. M. Rowe, J. LaRock, S. Singhal[1]

[1]IPA Fellow

The Reactor Radiation Division was granted support starting in FY79 under the NBS Competence Building Program to develop new and advanced instrumentation and scientific applications in neutron scattering from materials. The initial focus of this long-range competence building activity is small-angle neutron scattering (SANS) and its potential for unique applications in the polymer and biological sciences, solid state physics and magnetism, metallurgy and materials science, and in the microscopic nondestructive testing of bulk materials. Future activities will include the development of improved measurement capability to exploit new scientific opportunities in high-resolution, variable wave-vector neutron spectroscopy.

Some activities and accomplishments during the past year include:

- Completion of the detailed design of the entire SANS facility (excluding the multiple-sample control and alignment system). All collimating shielding and evacuated flight path components are completed or under construction. Installation has begun and is expected to be completed this coming winter.

- Successful testing of the first area detector for the SANS facility. The second, larger (65 x 65 cm) detector is expected to be delivered by October this year.

- Completion of a major fraction of the data-acquisition system and interactive on-line data analysis network including technicolor graphics capability.

- Establishment of cooperative research activities on metallurgical applications with the Navy, State University of New York (SUNY), BNL, and the NBS Metallurgy Division.

- Support of expanded SANS research on polymers by the NBS Polymer Science and Standards Dívision and their university and industrial collaborators.

- Application of SANS combined with low-energy, inelastic scattering to studies of and magnetic correlations and interactions in spin glasses and magnetic superconductors.

- Initiated applications of SANS to study the kinetics of microstructural development in nickel-based superalloys which are used routinely in aircraft turbine-blade applications.

ADVANCED NEUTRON METHODS
Task 51102

C. Glinka, N. Berk, J. M. Rowe, J. LaRock, S. Singhal[1]

[1]IPA Fellow

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- Application of SANS combined with low-energy, inelastic scattering to studies of and magnetic correlations and interactions in spin glasses and magnetic superconductors.

- Initiated applications of SANS to study the kinetics of microstructural development in nickel-based superalloys which are used routinely in aircraft turbine-blade applications.

Other Activities of the
Reactor Radiation Division

Invited Talks

Neutron Sources for Field Neutron Radiographic Applications
Conference of the American Society for Nondestructive Testing, St. Louis, Missouri
D. A. Garrett
October 1979

Neutron Scattering Instruments Equipped With Position-Sensitive Detectors
National Institutes of Health Instrumentation Symposium, Bethesda, Maryland
A. Wlodawer
October 4, 1979

Application of Derivative Lattices to the Indexing of Powder Patterns from Modulated Structures
Washington Crystal Colloquium, Geophysical Lab, Washington, D.C.
A. Santoro
October 26, 1980

Crystal Field Effects in Magnetic Superconductors
International Conference on Crystalline Electric Fields and Structural Effects in f-Electron Systems, Philadelphia, Pennsylvania
J. W. Lynn
November 12, 1979

Exchange and Crystal Field Excitations in RFe_2 and RCo_2 Compounds
International Conference on Crystalline Electric Fields and Structural Effects in f-Electron Systems, Philadelphia, Pennsylvania
N. C. Koon and J. J. Rhyne
November 13, 1979

Diffraction Studies of Propellant Ingredients
U.S. Army Armament R and D Command, Dover, New Jersey
H. J. Prask
December 1979

Spin Waves and Crystal Field Excitation in Rare Earth Laves-Phase Compounds
University of Rhode Island, Physics Department Colloquium, Kingston, Rhode Island
J. J. Rhyne
December 14, 1979

Diffraction Patterns from Modulated Structures
Centre National de la Reserche Scientifique, Laboratoire de Cristallographic, Grenoble, France
A. Santoro
January 8, 1980

Neutron Scattering Studies of Rotation-Translation Coupling in Orientationally Disordered Ionic Crystals
Gordon Research Conference on Orientational Disorder in Crystals, Santa Barbara, California
J. J. Rush
January 16, 1980

Preferential Atomic Ordering and Magnetism in $R_6(Fe_{1-x}Mn_x)_{23}$ Compounds
University of Pittsburgh, Chemistry Department, Pittsburgh, Pennsylvania
K. Hardman
January 17, 1980

Theory of Diffusion-Mediated Excitonic Processes in Molecular Crystals: Magnetic Field Dependence of Fluorescence and EPR
Statistical Physics Seminar, National Bureau of Standards, Gaithersburg, Maryland
N. Berk
January 24, 1980

Why Least-Squares . . . and Why Not?
Washington Crystal Colloquium, Washington, D.C.
E. Prince
February 1980

Methyl Reorientation and Quantum Mechanical Tunneling in Solid Nitromethane
Westinghouse Research Corporation, Pittsburgh, Pennsylvania
S. F. Trevino
February 7, 1980

Exchange and Crystal Field Effects in RFe_2 and RCo_2 Compounds
Solid State Colloquium, University of Maryland, College Park, Maryland
J. J. Rhyne
February 13, 1980

On the Existence of an "Orientational Glass" State in Mixed Crystals of $(KCN)_x(KBr)_{1-x}$
National Bureau of Standards, Thermophysics Division, Gaithersburg, Maryland
J. M. Rowe
February 14, 1980

Phonons in Metal Hydrogen Systems
Solid State Physics Seminar, University of Illinois, Urbana, Illinois
A. Magerl
March 1980

Magnetic Inelastic Neutron Scattering Studies of Rare Earth Metals and Laves-Phase Compounds
Indo-U.S. Conference on the Science and Technology of Rare Earth Materials, Cochin, India
J. J. Rhyne
March 3, 1980

Magnetism in Amorphous Rare Earth Alloys
Indo-U.S. Conference on the Science and Technology of Rare Earth Materials, Cochin, India
J. J. Rhyne
March 4, 1980

High Resolution Neutron Powder Diffraction and Small Angle Neutron Scattering at the National Bureau of Standards
Winter Meeting of the American Crystallographic Association, Eufala, Alabama
E. Prince, A. Santoro, and C. J. Glinka
March 19, 1980

Theory and Design of Instrumentation for Bridge Inspection
NBS - Mechanical Failure Prevention Group, Gaithersburg, Maryland
D. A. Bracher, D. A. Garrett, and C. Heller
April 1980

Instrumentation and Procedures for Rapid Data Collection in Neutron Crystallography
Argonne National Laboratory, Argonne, Illinois
A. Wlodawer
April 16, 1980

Structure of Ribonuclease-A Studied by X-ray and Neutron Diffraction
University of Chicago, Department of Theoretical Biology, Chicago, Illinois
A. Wlodawer
April 17, 1980

Neutron Radiography of Antiquities
Joint NBS Smithsonian Series, NBS, Gaithersburg, Maryland
D. A. Garrett
May 1980

Combined X-ray and Neutron Diffraction Studies on Ribonuclease-A
Washington Crystal Colloquium, Geophysical Lab, Washington, D.C.
A. Wlodawer
May 2, 1980

Spin Wave Scattering from $RbMnCl_3$
University of Rhode Island, Physics Department, Kingston, Rhode Island
H. A. Alperin
May 2, 1980

Neutron Scattering Research on Hydrogen in Metals
Belgium Atomic Energy Commission, Mol, Belgium
J. M. Rowe
June 10, 1980

The Use of Neutron Scattering Technique to Study Hydrogen in Metals
National Bureau of Standards, Chemical Stability and Corrosion Division, Gaithersburg, Maryland
K. Hardman
June 23, 1980

Neutron Diffraction Analysis of Ribonuclease
Birkbeck College, London, England
A. Wlodawer
June 27, 1980

Neutron Diffraction Analysis of Ribonuclease
Institut Laue-Langevin, Grenoble, France
A. Wlodawer
July 3, 1980

Neutron Scattering Studies of Translation-Rotation Coupling Crystals
Institut Laue-Langevin, Grenoble, France
J. M. Rowe
July 3, 1980

Neutron Diffraction and Small-Angle Scattering as Nondestructive Probes of the Microstructure of Materials
Conference on the Mechanics of Nondestructive Testing, Virginia Polytechnic Institute, Blacksburg, Virginia
C. J. Glinka
September 11, 1980

Technical and Professional Committee Participation and Leadership

American Crystallographic Association
Apparatus and Standards Committee, E. Prince, Member

American National Standards Committee, N-17
R. S. Carter, Secretary

American Society for Nondestructive Testing
Penetrating Radiation Committee, D. A. Garrett, Voting Member

Research Committee, D. A. Garrett, Voting Member

Personnel Qualifications Committee, D. A. Garrett, Voting Member

Spring Conference, D. A. Garrett, Chairman

American Society for Testing and Materials
E-7.05: Nondestructive Testing - Neutron Radiography, D. A. Garrett, Secretary

ANS-15 Standards for Research Reactors
T. M. Raby

Argonne National Laboratory
Program Review Committee for the Intense Pulsed Neutron Source, J. M. Rowe, Chairman

Argonne National Laboratory and Department of Energy
Facilities Review Panel on Intense Pulsed Neutron Sources, J. M. Rowe, Chairman

Conference on Magnetism and Magnetic Materials
Advisory Committee, J. J. Rhyne, Member

Department of Energy
Neutron Scattering Review Panel, J. J. Rush, Member

Panel to Review U. S. Pulsed Neutron Scattering Research Facilities, J. J. Rush, Member

Fourteenth Rare Earth Research Conference
Spedding Award Committee, J. J. Rhyne, Member

Gordon Conference on Orientational Disorder in Crystals
Reorientation Phenomena in Crystals Session, J. M. Rowe, Discussion Leader

International Conference on Crystalline Electric Fields and Structural Effects in f-Electron Systems
Lattice Effects I Session, J. J. Rhyne, Session Chairman

International Conference on Ternary Superconductors
Program Advisory Committee, J. W. Lynn, Member

Magnetism Letters
Editorial Board, J. J. Rhyne, Member

March Meeting of the American Physical Society
Molecular Dynamics of Simple Liquids Session, J. M. Rowe, Session Chairman

Oak Ridge National Laboratory
National Center for Small Angle X-ray and Neutron Scattering
Program Review Committee, J. J. Rhyne, Member

National Bureau of Standards
Radiation Safety Task Force Review Panel, J. J. Rush, Member

Research Advisory Committee, J. J. Rush, Chairman

Publications

A Robust/Resistant Technique for Crystal Structure Refinement
W. L. Nicholson and E. Prince
Acta Cryst. A (submitted)

Texture, Nondestructive Characterization
H. J. Prask and C. S. Choi
Ency. Matls. Sci. and Eng. (submitted)

Comparison of Profile and Integrated Intensity Methods in Powder Refinement
E. Prince
J. Appl. Cryst. (submitted)

Use of Derivative Lattices in the Indexing of Powder Patterns
A. Santoro
Acta Cryst. (submitted)

Preliminary Investigation of a New X-ray Film
S. Abrahamsson, O. Lindqvist, L. Sjölin, and Alexander Wlodawer
J. Appl. Cryst. (submitted)

Molybdoarsinate Heteropoly Complexes. The Structure of the Hydrogentetramolybdodimethylarsinate (2-) Anion by X-ray and Neutron Diffraction
K. M. Barkigia, L. M. Rajkovic-Blazer, M. T. Pope, E. Prince, and C. O. Quicksall
Inorganic Chemistry (in press)

Phase Transitions in Ammonium Nitrate
C. S. Choi, H. J. Prask, and E. Prince
J. Appl. Cryst. (in press)

Refinement of Dipara-anthracene
C. S. Choi and P. L. Marinkas
Acta Cryst. (in press)

Powder Neutron Diffraction Study of Chemically Prepared β-PbO_2
Peter D'Antonio and A. Santoro
Acta Cryst. (in press)

Neutron Diffraction and Small-Angle Scattering as Nondestructive Probes of the Microstructure of Materials
C. J. Glinka, H. J. Prask, and C. S. Choi
Proceedings of the Conference on Mechanics of Nondestructive Testing (to be published by Plenum Press)

Preferential Ordering of Mn and Fe Atoms in $Y_6(Fe_{1-x}Mn_x)_{23}$
K. Hardman, W. J. James, and W. B. Yelon
Journal of Physics and Chemical Solids (in press)

Structural Investigation of $Th_6Mn_{23}D_{16}$ by Neutron Diffraction
K. Hardman, J. J. Rhyne, K. Smith, and W. E. Wallace
Journal of the Less Common Metals (in press)

Neutron Inelastic Scattering Study of C_2H_4 Adsorbed on Raney Nickel
R. D. Kelley, R. R. Cavanagh, J. J. Rush, and T. E. Madey
Surface Science (in press)

On the Observation of Low Energy Excitations in NbD - A Simple Lattice Dynamical Model
A. Magerl, J. M. Rowe, and D. Richter
Phys. Rev. B (in press)

On the Existence of an Orientational Glass State in $(KCN)_x(KBr)_{1-x}$ Mixed Crystals
K. H. Michel and J. M. Rowe
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Nondestructive Testing of Armament-System Components by Means of Neutron Diffraction
H. J. Prask, C. S. Choi, and S. F. Trevino
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Magnetic Inelastic Neutron Scattering Studies of Rare Earth Metals and Laves-Phase Compounds
J. J. Rhyne
Proc. of the Science and Technology of Rare Earth Materials (in press)

Magnetic Materials
J. J. Rhyne
Article for the Encyclopedia of Physics, ed. by R. G. Lerner and G. L. Trigg, Addison-Wesley Publishing, Reading, MA (in press)

Coherent Neutron Scattering Study of the Vibrations of Interstitial Deuterium in α-$VD_{0.7}$
J. J. Rush, J. M. Rowe, C. J. Glinka, N. Vagelatos, and H. E. Flotow
Phys. Rev. (in press)

Neutron Scattering Study of Hydrogen Vibrations in Polycrystal and Glassy TiCuH
J. J. Rush, J. M. Rowe, and A. J. Maeland
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A. Santoro, A. D. Mighell, and J. R. Rodgers
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Lattice Relationships: The Determination of Matrices That Will Relate Any Given Pair of Lattices
A. Santoro, A. Mighell, and J. Rodgers
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Neutron Powder Diffraction Study of the Structure of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$
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T. W. Dombeck, J. W. Lynn, S. A. Werner, T. Burn, J. Carpenter, V. Krohn, and R. Ringo
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Neutron Crystal-field Spectroscopy of $CeD_{2\ 12}$
C. J. Glinka, J. M. Rowe, G. G. Libowitz, and A. Maeland
Journal of Physics: C 12, 4229 (1979)

Vibrational Spectroscopy of Adsorbed Species on Nickel by Neutron Inelastic Scattering
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Magnetic Properties of the Superconducting Alloy System $(Ce_{1-c}\ Ho_c)Ru_2$ - A Neutron Scattering Study
J. W. Lynn and C. J. Glinka
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Amorphous Magnetic Materials - Chapter 16
J. J. Rhyne
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Neutron Scattering Study of the Dynamics of $KCN_{.5}KBr_{.5}$
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Crystalline Electric Fields and Structural Effects in f-Electron Systems, edited by J. E. Crow, R. P. Guertin, and T. W. Mihalisin, Plenum Publishing, New York, p. 125 (1980).

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Magnetic Correlations and Crystal Field Levels in the Superconductor $(Ce_{.73}Ho_{.27})Ru_2$
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RPA Theory of Magnetic Excitations in Rare Earth-Transition Metal Compounds: Application of $ErCo_2$ and $ErFe_2$
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Neutron Scattering Studies of Hydrides of the Laves-Phase Rare Earth Compounds RFe_2
G. E. Fish, J. J. Rhyne, T. Brun, P. J. Viccaro, D. Niarchos, B. D. Dunlap, G. K. Shenoy, S. G. Sankar, and W. E. Wallace
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A. Santoro and Alexander Wlodawer
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Division Seminars

Recent Developments in Neutron Instrumentation at the Institut Laue-Langevin
T. Springer
Institut Laue-Langevin, Grenoble, France
October 4, 1979

Neutron Scattering on Magnetic Moments in Intermetallic Compounds
M. Loewenhaupt
Institut für Festkörperforschung, KFA Jülich, West Germany
November 16, 1979

Rotational Tunnelling in Solids
A. Huller
Kernforschungsanlage Jülich, West Germany
January 22, 1980

Theory of Strain Dipoles and Orientational Ordering
K. H. Michel
University of Antwerp, Antwerp, Belgium
January 22, 1980

The Magnetic Structure of Neodymium--A Hard Case to Solve
B. Lebech
Risø National Laboratory, Denmark
February 5, 1980

Single Chain Structure Factor from Combined Small Angle Neutron and Small Angle X-ray Scattering
S. J. Bai
University of Michigan, Ann Arbor, Michigan
February 8, 1980

Light Scattering Studies of KH_2PO_4 Near the Ferroelectric Transition in An Applied Field
R. Gammon
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland
February 12, 1980

Competing Interactions and Order-Disorder Phenomena in Ammonium Halides
C. Garland
Massachusetts Institute of Technology, Cambridge, Massachusetts
March 10, 1980

Hydrogen Diffusion in Metals
H. Wipf
Technical University of Munich, Munich, West Germany
April 18, 1980

Computer Simulation of Elastic Crystal Phases
M. Klein
National Research Council, Ottawa, Canada
April 30, 1980

Neutron Scattering Study on Benzene and Toluene Adsorbed on Graphite Basal Planes
M. Monkenbusch
Institut für Festkörperforschung, Jülich, West Germany
June 2, 1980

SANS Study of Hot Stretched Polystyrene
Francois Boue
Laboratoire Leon Brillouin, France
July 1980

Diagnostics of Neutron Beams
D. Alger
University of Missouri, Columbia, Missouri
July 1980

Some Recent Developments in Neutron Scattering Sources and Research in West Germany
W. Schmatz
Kernforschungsanlage, Karlsruhe, West Germany
July 9, 1980

Three-axis Neutron Spectrometers at the ILL
R. Pynn
Institut Laue-Langevin, Grenoble, France, and Brookhaven National Laboratory, Upton, New York
August 1, 1980

Neutron Scattering at Jülich
D. Richter
Kernforschungsanlage Jülich, West Germany
August 18, 1980

Books

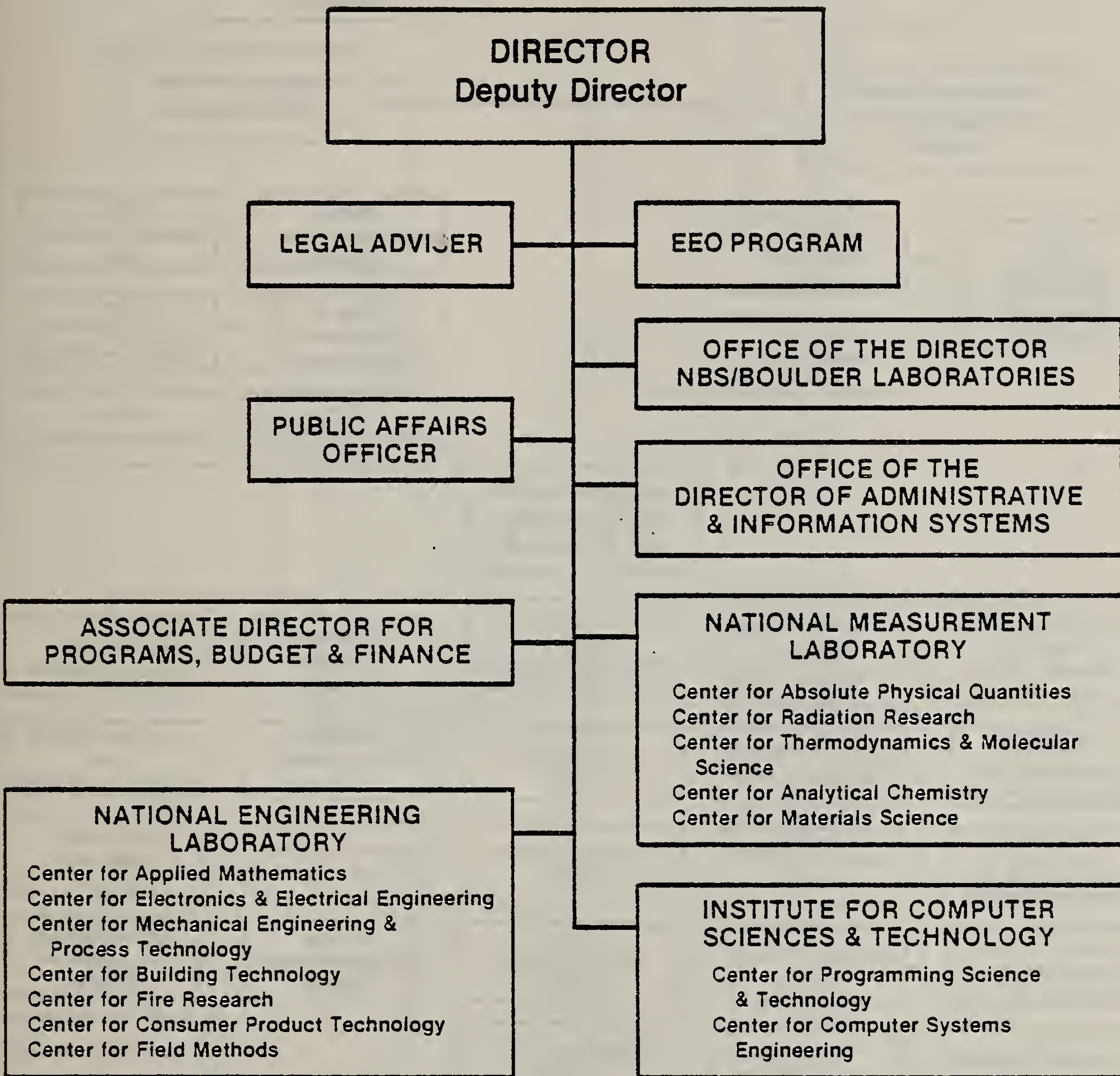
The Rare Earths in Modern Science
Edited by G. J. McCarthy, J. J. Rhyne, and H. Silber
Plenum Publishers, New York, 647 pages (1980)
Proceedings of the Fourteenth Conference on Rare Earth Research, Fargo, North Dakota, June 25-28, 1979

Special Reports

Report of the Facilities Review Panel to the Department of Energy on Intense Pulsed Neutron Sources
R. R. Neal, J. J. Rush, coauthor
Report to the Assistant Secretary for Research of the Department of Energy (July 1980)

Summary Report on Some Areas of Scientific Opportunity for the National Bureau of Standards
J. J. Rush and members of the Research Advisory Committee
Research Advisory Committee Report to the Director (December 1979)

APPENDIX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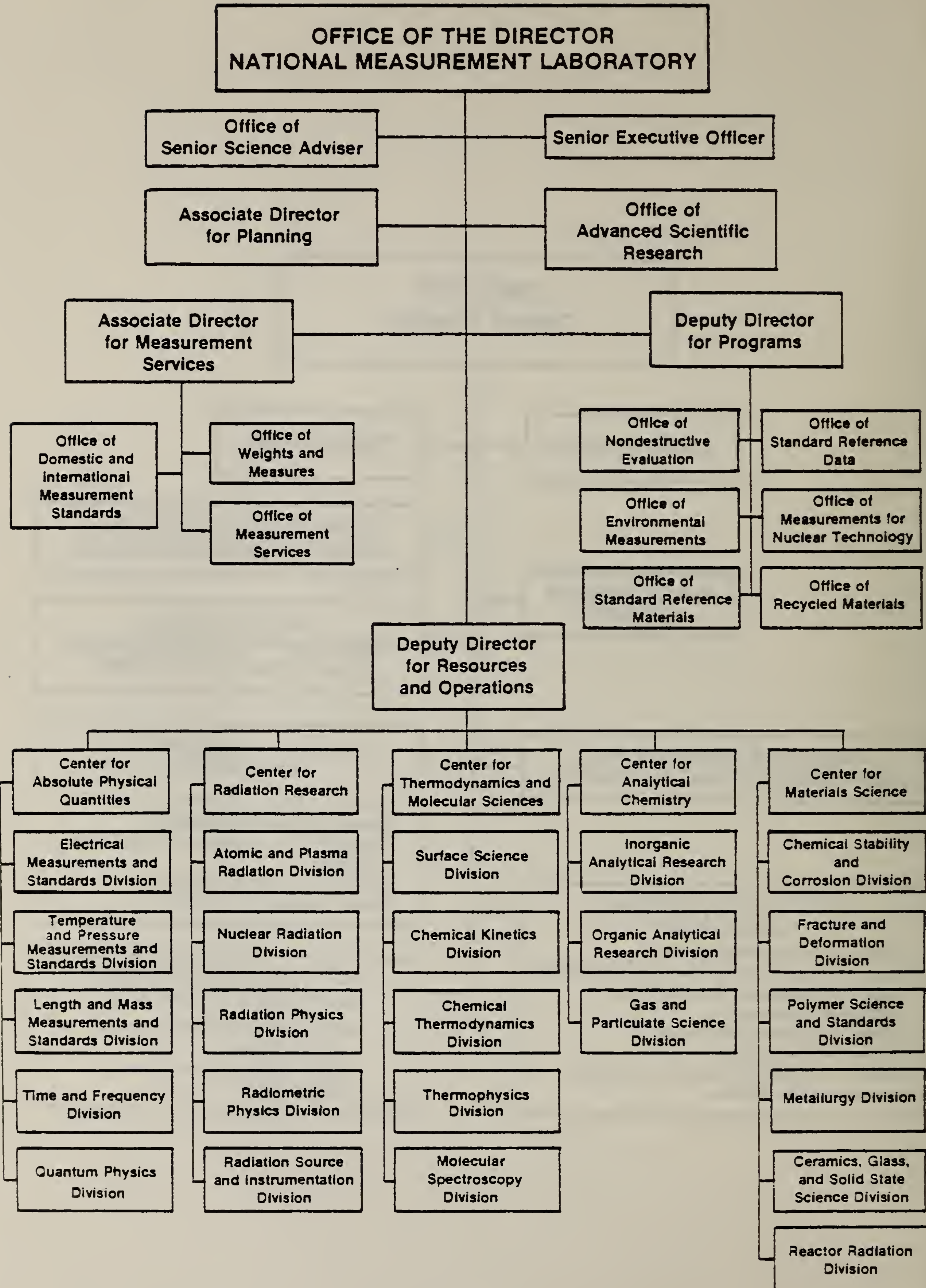
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11. Contract/Grant No.

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13. Type of Report & Period Covered

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The Center for Materials Science is part of the National Measurement Laboratory, one of the principal laboratories comprising the National Bureau of Standards. The Center is organized in six Divisions, each having responsibility in different areas of materials science appropriate to the major classes of materials -- metals, polymers, and ceramics and glass. These Divisions vary in their balance between theory and experiments, between direct standards work and research, and in their orientation toward industrial and Government needs and the needs of other components of the scientific and technical community. This volume summarizes the technical research activities and accomplishments of the six Divisions of the Center for Materials Science for Fiscal Year 1980.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Center for Materials Science; Ceramics Glass and Solid State Science Division; Chemical Stability and Corrosion Division; Fracture and Deformation Division; FY80 Technical Activities; Metallurgy Division; Polymers Science and Standards Division; Reactor Division

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