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# Technical Note

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**RESEARCH ON CRYSTAL GROWTH  
AND DEFECT CHARACTERIZATION  
AT THE NATIONAL BUREAU OF STANDARDS  
DURING THE PERIOD JULY TO DECEMBER 1962**



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**U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS**

## THE NATIONAL BUREAU OF STANDARDS

### Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. Research projects are also performed for other government agencies when the work relates to and supplements the basic program of the Bureau or when the Bureau's unique competence is required. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

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The results of the Bureau's research are published either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau publishes three periodicals available from the Government Printing Office: The Journal of Research, published in four separate sections, presents complete scientific and technical papers; the Technical News Bulletin presents summary and preliminary reports on work in progress; and the Central Radio Propagation Laboratory Ionospheric Predictions provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: Monographs, Applied Mathematics Series, Handbooks, Miscellaneous Publications, and Technical Notes.

A complete listing of the Bureau's publications can be found in National Bureau of Standards Circular 460, Publications of the National Bureau of Standards, 1901 to June 1947 (\$1.25), and the Supplement to National Bureau of Standards Circular 460, July 1947 to June 1957 (\$1.50), and Miscellaneous Publication 240, July 1957 to June 1960 (includes Titles of Papers Published in Outside Journals 1950 to 1959) (\$2.25); available from the Superintendent of Documents, Government Printing Office, Washington 25, D.C.

# NATIONAL BUREAU OF STANDARDS

*Technical Note 174*

ISSUED MARCH 15, 1963

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Edited by H. Steffen Peiser

National Bureau of Standards

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

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Abstract

The National Bureau of Standards has embarked on a special program, partly supported by the Advanced Research Projects Agency, to unify and accelerate its research on the growth and characterization of crystals. This work will provide theory on the mechanism of crystal growth, experimental techniques for growth and study of crystals, interpretive analysis of observations on crystals examined by diverse methods, and data from the measurement of defect-sensitive properties of crystals. Just as the results of this work are to benefit research and, ultimately, technology in chemistry, solid-state physics, metallurgy, mineralogy, electronics, and engineering, so the NBS program is most widely based on collaborative efforts of twelve technical divisions of the Washington and Boulder Laboratories.

This note describes principally the individual NBS research activities during July to December 1962 coupled with statements on the most immediate plans at the end of that period. An introductory section is followed by two other brief general sections describing the program area and the NBS background interest in the field of crystal growth and characterization. A list of NBS publications appertaining to the period under review and a partial list of participants are appended.

1. INTRODUCTION

A surprising number of major programs in research and technology have in common their dependence upon the solution of basic material problems in the production and characterization of specific crystals. Yet, there is rather little cross-fertilization in ideas between scientists investigating growth and the characterization of crystals. Many would not regard themselves as crystal specialists at all, but as chemists, physicists, mineralogists, electronic or mechanical engineers who just happen to face a problem in crystallography barring their own individual progress.

Aware of the benefits to be expected from a more specialized professional attitude towards the problems of crystal growth, coupled with the establishment of recognized channels of dissemination of research information, C. F. Yost, Assistant Director for Materials Sciences, Advanced Research Projects Agency, has encouraged the initiation of co-ordinated programs in this field within large research institutions having an established competence in crystal science. In particular, at NBS where the opportunity exists to build upon such competence as well as on a unique and relevant background in precise measurement, he has worked out with I. C. Schoonover, NBS Associate Director, a program for accelerated research in those areas of crystal research that are judged to be of critical importance to the entire field of materials research. This NBS/ARPA plan has been accepted by the two agencies concerned and was put into operation in June 1962.

This report attempts to cover the results of all NBS work on growth and characterization of crystals from July to December 1962. The majority of this research is NBS-supported and, indeed, might have proceeded along precisely the same lines even if the NBS/ARPA program had not been established. It is true, nevertheless, that the individual scientists concerned may have appreciated the loose cohesion into a "Crystal Group" through which informal colloquia have been held; distinguished guest consultants and lecturers have visited NBS from well-known outside institutions and universities; and current research

papers, considered by R. L. Parker to be of critical significance, have been circulated. Summaries of many new research projects are included that could not have been started or could not have proceeded at their present speed had it not been for the ARPA financial support which is hereby acknowledged. Since it is the aim of this report to summarize the scientific work no further reference will be made to the type of financial support received for individual projects.

No part of the NBS/ARPA research program is classified. A central reprint file is not kept, but in most cases reprints can be obtained from the authors. Similar Technical Notes will be published at six-monthly intervals for the duration of this NBS/ARPA research program.

The editor of this report, H. S. Peiser, besides his principal duties as Crystal Chemistry Section Chief, acts as co-ordinator of the NBS/ARPA crystal growth and characterization research program. He is pleased at all times to give information about the program to enquirers from within NBS and also those from outside. Above all he welcomes opportunities of arranging contacts with universities and other research institutions active in this field, in the U. S. or abroad. Finally he hopes to encourage distinguished scientists wishing to join our Crystal Group as guests over a period of some months in one of our active projects in which they have a special personal interest.

## 2. BACKGROUND

When the principal responsibility of the National Bureau of Standards to "provide the central basis for a complete consistent system of physical measurement adequate for the expanding national activity in scientific research" is applied to the materials field in general and crystals, the most perfectly atomically ordered form of matter, in particular, there can be no doubt that the highest scientific understanding of the physics and chemistry of materials is required, coupled with an ability to measure material properties. So sensitive, however, is the technologically significant behavior of crystals to minute differences in chemical composition and to occasional departures from perfect regularity in lattice structure that to fulfill its mission the NBS needs to be at the forefront of crystal research.

It is no wonder therefore that throughout the technical divisions of the NBS, groups of scientists have long been engaged in research and measurements on crystals. Perhaps the best known group, under the leadership of H. F. McMurdie, has developed from the crucial support it has given to ceramic and glass technologies. Outstanding, too, have been the contributions of H. C. Vacher's group to metallurgical systems. Separate again has been C. P. Saylor's team that has pursued so successfully the crystal-growth process as a means for purification of phases. H. F. Stimson in his fundamental studies of drifts in the triple-point water cell became of necessity interested in crystal growth. His basic aim was to produce a reliable temperature standard, yet his requirements led him into a difficult problem in thermodynamics of the crystallization process; a problem incidentally that remains to some extent for further study at NBS.

In this way, one could cite almost thirty groups at NBS which have made significant crystallographic contributions before the start of the NBS/ARPA program. Most of these were actively engaged in related work at the outset of this program and, evidently, their work was justifiable under the general NBS mission. Even in the center of our present program area R. L. Parker had developed the vapor growth technique of growing for instance potassium single crystals to the point where his experimental results critically differentiated between rival theories of growth mechanisms. Hoffman and Lauritzen had been recognized for their chain-folding theories of polymer crystal growth; and Wachtman had laid the foundations to his basic theories on the internal-friction effects caused by point defects in crystals. However, to give examples is almost invidious for the many other instances left unmentioned. The important point to make here is that under its own mission NBS had flourishing crystallographic research activities on the successes of which it is the plan of the NBS/ARPA program to build with the help of the existing staff as well as with new promising participants drawn to NBS by the opportunities now offered.

There is one more point that has to be made, because it is believed to be of great



importance. Much of the research published in crystallography suffers from a lack of careful characterization of samples studied and equally from inadequate accuracy in measurement. Again, to give an example reference is made to Section 5.14 of this report. Specific resistance is the basic property on which the quality of most semiconductor crystals is supposed to be assessed. Yet the measurement techniques used not only lack precision but there are unexplained inconsistencies that make a uniform measuring system unavailable in a most important area of modern technology.

If there is any feature that should - and, as we believe, does - describe above all others research at our national standards institution, it is the interest in really careful measurements on painstakingly identified objects. It is our aim to apply this attitude to research on crystals.

### 3. DESCRIPTION OF THE PROGRAM AREA

For the purpose of the NBS/ARPA program it has been helpful to define crystal growth broadly to include nucleation processes. The size of the crystals has not been a primary consideration in judging relevance of a project. Moreover, dissolution, the complementary process to growth, has been included.

The characterization of crystals is defined somewhat narrowly as the detection and definition of chemical impurities and lattice-structural defects. We tended to exclude studies of properties characteristic of the phase as such and not sensitive to the presence of defects or dislocations. Crystal-structure analysis thus is an example of an area which, though strongly pursued at NBS by S. Block, his collaborators, and others, has not been greatly concerned with the NBS/ARPA program.

Within the field of definition we place emphasis on those experimental and theoretical projects which are relevant to the basic physics of the mechanism of crystal growth; those that are concerned with possibly new techniques of crystal growth; on those that relate crystal characterization to growth processes; and on those that are in the NBS areas of special competence such as physical measurement at or near the maximum attainable precision.

In assembling this report many close decisions of inclusion and exclusion had to be made. Some of these may even appear arbitrary, but it is hoped some logical reasons can usually be offered. For example, if some portion of a project is relevant we have encouraged the inclusion of a brief balanced description of the project, without unduly slanting it to the aims of the report as a whole.

Subdividing the projects under main headings and deciding on an order of presentation has been equally difficult though clearly far less important. Even when it was decided to have just two simple main headings, Crystal Growth (Section 4) and Crystal Characterization (Section 5), there were some borderline sub-sections that would have fitted either. Rather than split descriptions into too many small fragments partial inconsistencies have been consciously permitted. No perfect order of presentation of sub-sections could exist and no defense will be made of the order chosen. The best one can hope for is that some aspects of that order will appear logical to the reader.

### 4. CRYSTAL GROWTH

#### 4.1. High-Temperature Crystal Growth

##### F. Ordway, Crystal Growth Section

Measurements of temperatures in the melt and the growing crystals during the Verneuil process were made, using Ir-Rh thermocouples, on rutile and sapphire. Crystals of rutile were grown at a wide range of rates, and the study of their dislocation contents, as revealed by etch pits, was begun.

The plasma furnace for the Verneuil technique was modified to exclude outside air, permitting complete control of the atmosphere around the growing crystal. The apparatus was used to grow small crystals of  $TiO_2$  (rutile),  $ZrO_2$  (CaO stabilized),  $Al_2O_3$ , and  $Y_2O_3$ .

Chromic oxide of suitable particle size, aggregation and purity for feed to the Verneuil apparatus was prepared, and single crystals were grown. Crystals of  $\text{YBO}_3$  (vaterite form) were grown for structure analysis. Manganites of Ho, Er, Lu, and Y, and small crystals of  $\text{CsPbCl}_3$  were grown for electrical measurements.

A supply of  $\text{ThO}_2$  was purified for eventual attempts at crystallization from the melt. This material was of such purity as to demand ultratrace analyses of higher sensitivity than the spectrographic methods now available at NBS.

#### 4.2. Crystal Growth and Structure Studies on Rutile

D. E. Roberts and M. I. Cohen

Solid State Physics Section

More than half of the projects in the Solid State Physics Section are in need of pure, reduced and doped rutile,  $\text{TiO}_2$ . It is the principal objective of the work here described to satisfy this need. At the moment the work is concerned with molybdenum-doped crystals of sufficient homogeneity for magnetic and optical studies.

One project is in need of CdTe crystals of a given conductivity. Equipment is assembled for treatment of such samples.

Recently obtained X-ray equipment is now in the testing stage. This equipment will be used to orient samples and to measure lattice constants as a function of temperature, especially around transition points (Curie and Neel temperatures).

#### 4.3. The Growth of Dislocation-Free Metal Crystals from the Melt

T. H. Orem, Metal Reactions Section

R. L. Parker, Metal Physics Section

The purpose of this project is to grow dislocation-free metal crystals by the Kyropoulos technique.

Two recent efforts in this field, one theoretical by Jackson [Phil. Mag. 8th Ser. 17, p. 1117 (1962)], the other experimental by Howie and Elbaum [Phil. Mag. 8th Ser. 6, p. 1227 (1961)] indicate that by proper control of size, shape, purity, orientation and pulling speed it is possible to grow sizable metal crystals with no dislocations. In the latter work, aluminum crystals in the form of rods 1 mm in diameter were grown with no dislocations over a small area. Jackson emphasized the need for purity of the starting material, particularly in freedom from very small extraneous foreign particles or larger than atomic dimensions. We are planning to set up a specially designed crystal puller with its necessary auxiliary equipment. Our initial work will probably be on aluminum of 6-9's purity.

#### 4.4. Kinetics of Growth of Crystals from the Melt

R. L. Parker, Metal Physics Section

The aim of this new project is to investigate the kinetics of the growth of crystals from the melt and in particular to study the role of interface temperature and structure.

A new and very promising experimental method for obtaining interface temperature has just been suggested by Tiller [J. Chem. Phys. 37, 841 (1962)]. This technique should permit the temperature at the interface to be accurately determined in a wide range of systems. A bibliography of the literature in this field, including prior experimental attempts to obtain interface temperatures, has been assembled. We have been attempting to recruit a well qualified young scientist to work on this problem.



#### 4.5. Crystal Growth from Solution

J. L. Torgesen, A. T. Horton, and  
J. Strassburger, Crystal Chemistry Section

The following have been the three principal objectives:

- a.) To study the properties of single crystal specimens, both those of ultra-high purity and those purposely contaminated, by appropriate physical and chemical methods, correlating the properties with the nature and amount of impurities present.
- b.) By development of crystallization techniques and by the growth of large single crystals, to prepare specimens of inorganic and organic substances of extremely high purity, thus providing basic reference materials for research.
- c.) To conduct basic research relating to the mechanisms of crystal growth and impurity retention, especially to the circumstances that determine the extent to which minor constituents (impurities) in a liquid system are retained or rejected during the growth of a particular face of the solid phase of the dominant constituent.

During the period under review some improvements have been made in the crystal growth equipment (J. L. Torgesen, A. T. Horton and C. P. Saylor, 1963) shown in figure 1. Four temperature controllers have been rebuilt to provide individual d-c power supplies and compact rack-mounting of controller components (power panel, bridge, electronic relay, etc.) Specifications for equipment regularly to monitor and to record precise temperatures of up to ten crystal-baths in turn with each following a predetermined temperature program have been submitted to two commercial suppliers of recording equipment. An automatic warning system for temperature-control failure is to be incorporated in this equipment.

The electrolytic conductance of ionic solutions has been found to be a precise and sensitive measure of the concentration of these solutions at a given temperature in the saturation region. The measurements are made with an immersion conductance cell of new design (shown at the extreme right in figure 1) and they provide a means to monitor with great precision the growth conditions of supersaturation which obtain during the crystal-growth operation. Details on the design of conductance cells, the measurement procedures, and conductivity data for ammonium dihydrogen phosphate solutions are given in a current publication (Torgesen and Horton, 1963).

Studies on the retention of chromium in ammonium dihydrogen phosphate have continued by growth of these crystals from purposely contaminated solutions. The retention of chromium is strongly direction dependent, the impurity tends to concentrate in the tapered {100} faces in amounts dependent on the impurity content of the mother solution and the rate at which the crystals are grown. However, one recently completed experiment, in which growth was forced at extremely high supersaturations, shows chromium retained also on {101} faces. The quality of the specimens is poor, showing markedly irregular faces and the inclusion of mother liquor. High voltage X-ray diffraction patterns (see Section 5.13) taken from earlier specimens, in which but minute amounts of chromium are retained on {101}, show a marked increase in disorder in the chromium-contaminated portions of the crystal.

A phase study of the system oxalic acid/acetic acid/water at 50°C has been completed and will be submitted for publication. Anhydrous oxalic acid is shown to be the stable solid phase in equilibrium with solutions in acetic acid/water mixtures up to 5.2 percent water (see figure 2). Only moderate success has been achieved in the growth of oxalic acid dihydrate crystals from acetone-water mixtures. Recently harvested specimens await analysis and further study.

Slow growth of single crystal sodium chlorate (cubic class 23) produces a habit in which {100}, {110} and {111} are in evidence. Fast growth produces a singular cube habit. A recently completed run shows marked differences in the rate at which the several specimens grew, although growth was started from cubic seeds of essentially the same size. A study of dislocation densities in the several specimens awaits a search for a suitable

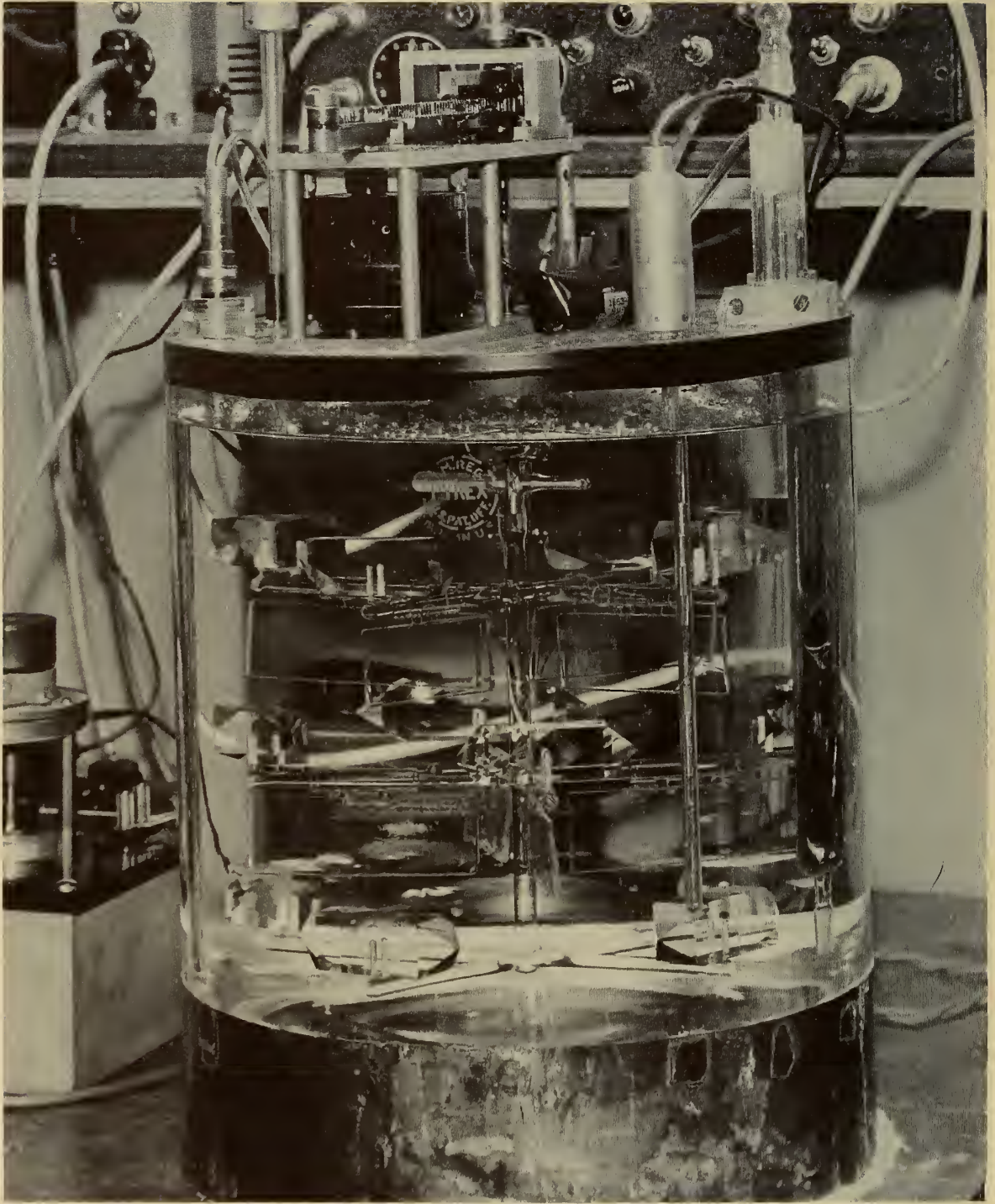


Figure 1. Crystal Growth Assembly



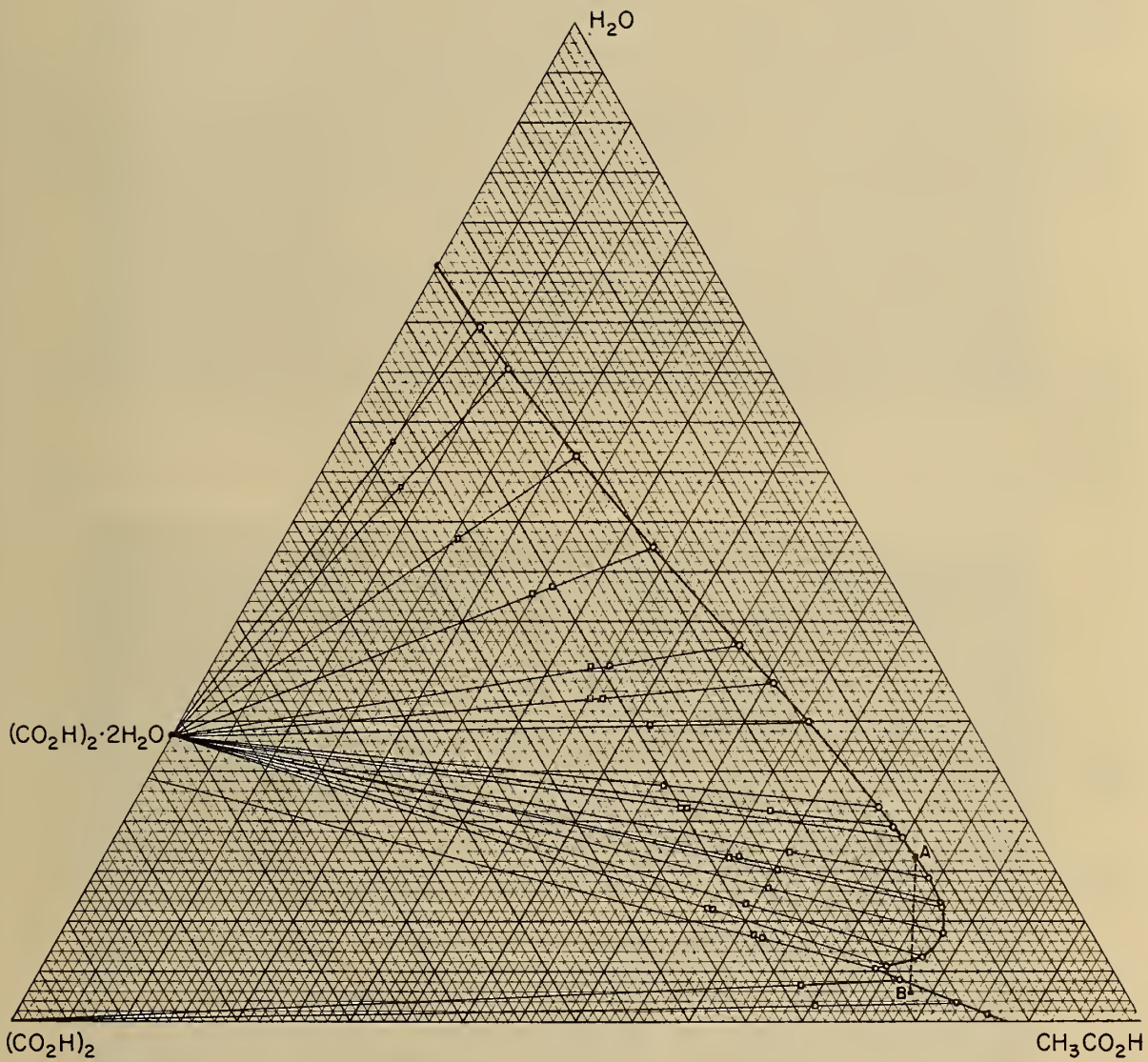


Figure 2. Phase Diagram. The System Oxalic Acid/Acetic Acid/Water, 50°C.



etchant and the preparation of thin specimens for diffraction microscopy by anomalous X-ray transmission.

Limited success is being achieved at this date in the growth of potassium chloride and potassium bromide from pure aqueous solutions. Potassium chloride seeds with a cube habit reverted in large measure to an octahedral habit in the early stages of growth at very low supersaturation. Subsequent growth has produced a cubic habit, but the crystal faces are rough. Potassium bromide is growing poorly, with some specimens exhibiting polycrystalline growth, and all specimens are milky, due apparently to the inclusion of mother solution. It is to be hoped that alkali halide crystals of good quality may be grown without heavy metal additives which are retained in the crystals. Comparison studies of solution-grown and melt-grown specimens are contemplated.

Steady-state diffusion processes are presently being studied with a view to developing techniques for the growth of crystals from solvents in which they are only sparingly soluble. Back-diffusion of the unwanted ions into source chambers is a problem which may be solved by proper design of baffling in the equipment. The growth of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in crude preliminary apparatus shows a strong tendency toward acicular habit (long, thin needles) and the formation of spherulites.

#### 4.6. Polymer Crystallization from Concentrated Solutions

E Passaglia, Polymer Physics Section

Most of the effort to date has gone into obtaining equipment and carrying out preliminary experiments. The crystallization of polypropylene from 5-10% solution in xylene on slow cooling from the boiling point to room temperature produces distinct well formed spherulites. Most of these are type I spherulites [F. J. Padden, Jr. and H. D. Keith, J Applied Phys 30, 1479 (1956)] although many are mixed forms. Work is now beginning on the measurement of the radial growth rate by microscopy, and on the bulk crystallization rate by dilatometry.

#### 4.7. Crystallization of Polyethylene Fractions

J. Powers, F. Quinn

Macromolecules Synthesis & Structure Section

and in part R. Neuman, Dielectrics Section

Growth rates of polyethylene spherulites from melts are being measured photographically as a function of molecular-weight distribution and of crystallization temperature. The data will be used in the calculation of surface free-energy values in a check of the Hoffman-Lauritzen chain-folding theories (Hoffman and Weeks, 1962).

The total isothermal-crystallization rate as measured dilatometrically is being compared with the rates of nucleation and formation of growth steps that can be resolved by hot-stage microscopy.

#### 4.8. Vapor-Phase Growth Kinetics of Potassium Crystals

R. L. Parker, Metal Physics Section

The purpose of this project is to study, by optical and other techniques, the vapor growth kinetics of metal crystals.

A paper on this subject (Parker 1962) appeared recently, the abstract of which reads as follows:

"Measurements of the growth rate of potassium (110) faces, for low vapor supersaturations between 3.1 and 0.11 (the lowest value studied) have given unit condensation coefficients for all supersaturations. This result is in agreement with the theory of Burton, Cabrera, and Frank and gives the values  $\beta C_0 = 1, \sigma_1 \leq 0.046$  for potassium. No evidence of

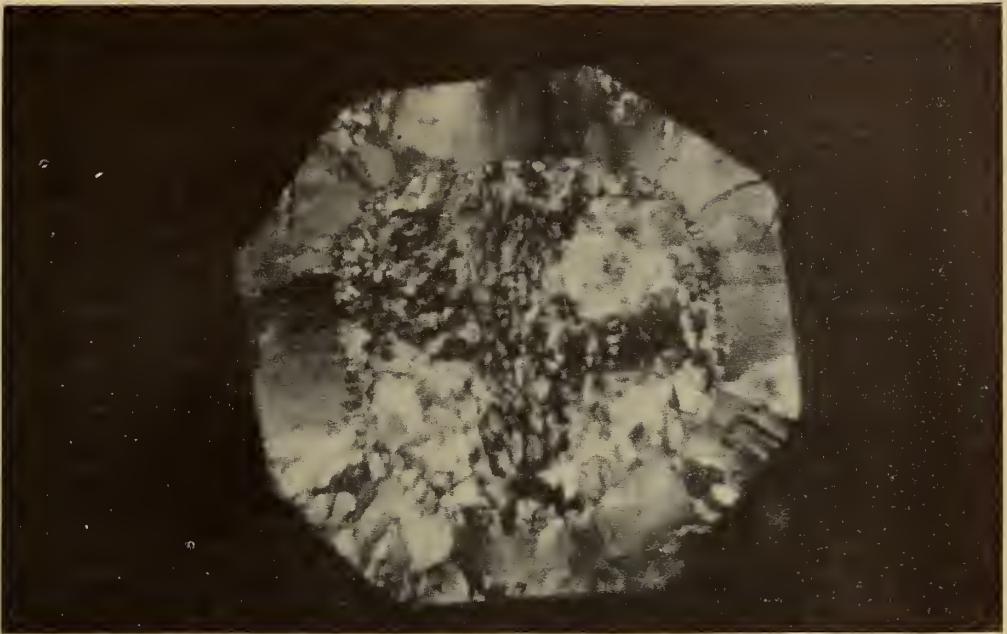


Figure 3. Transition of potassium nitrate at approximately 3 kilobars.  
Crystals in high-pressure phase are smaller than in low phase.

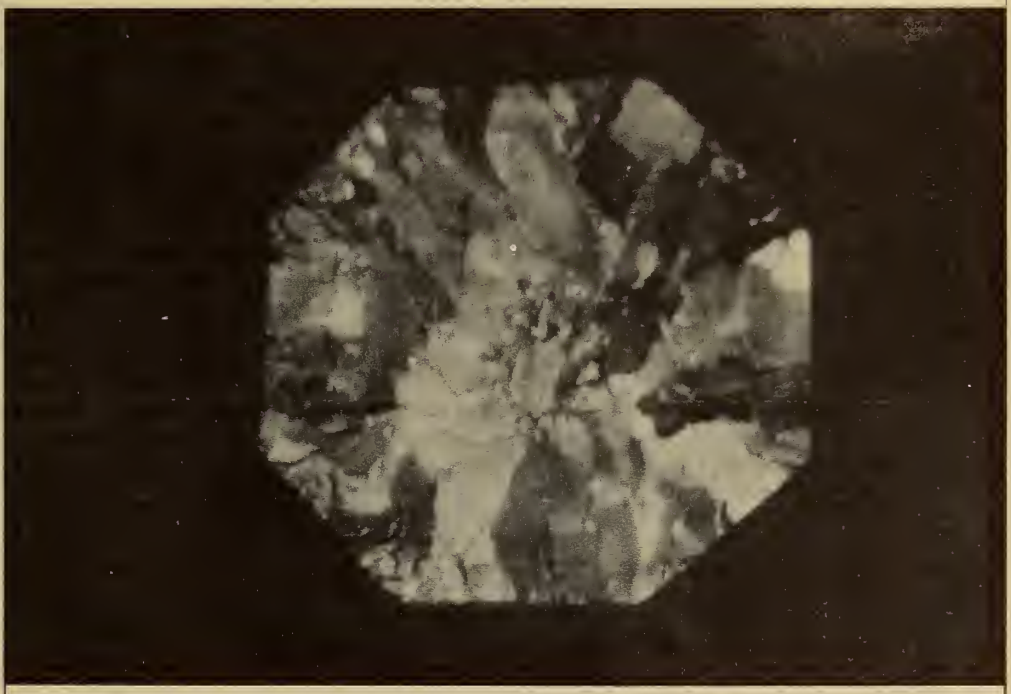


Figure 4. Potassium nitrate showing crystal orientation due to crystal growth along pressure gradient. Long direction of crystals parallel to pressure gradient.

two-dimensional surface nucleation was found. Careful attention to the reduction of impurities, through the use of ultra-high vacuum techniques, was shown to be necessary in studying this system. Results of earlier work by Hock and Neumann on potassium can be well described by an application of the Cabrera-Vermilyea theory of impurity effect, with an effective partial pressure of active gases of  $0.8 \times 10^{-11}$  mm Hg. In the present experiments this value is less than  $1.4 \times 10^{-13}$  mm Hg. The unit condensation coefficients are shown to be in disagreement with a theoretical prediction of Hirth and Pound."

A second paper was presented at the International Symposium on the Condensation and Evaporation of Solids, Sept. 12, 1962, in Dayton, Ohio, and will appear in a book of this title (Interscience Publishers). A mass spectrometer to permit the quantitative study of vapor phase growth rates in the presence of known amounts of dilute, active impurity gases is being procured and measurements should begin within a few months.

#### 4.9. Crystal Growth by Electrodeposition

F. Ogburn, Electrolysis & Metal Deposition Section

Preliminary studies indicate that electrodeposition under closely controlled conditions may provide an additional useful method for preparing single metal crystals.

Copper dendrites electrodeposited under one set of conditions exhibited a  $[110]$  preferred orientation in the growth direction, associated with easily discernable  $\{111\}$  side faces. Electrodeposited copper sheet also showed a  $[110]$  preferred orientation that improved with increasing thickness of deposit. The degree of double orientation seems to be very sensitive to impurities in the electrolyte. Both the dendrites and the sheet deposits showed twinning in a substantial majority of the grains. A start has been made with X-ray texture determinations by Buerger precession and Weissenberg methods.

#### 4.10. High-Pressure Microscopy to Study Crystal Transformation and Growth

A. Van Valkenburg, Crystallography Section

In the past six months a new technique has been developed (Van Valkenburg, 1962; Weir, Van Valkenburg, and Lippencott, 1962) to study phase transformations and crystal growth characteristics at pressures up to 100 kilobars using microscopic techniques. The technique involves a high pressure diamond cell and a polarizing microscope.

Studies have been conducted on several transitions that occur in the silver and copper halides at elevated pressures. One of the important features noted in the transitions is the continued crystal growth in the high-pressure phases after the transition has occurred. It has been noted that the rate of crystal growth appears to be greater where the pressure gradients are steep.

Crystal-growth phenomena have been studied in the compounds of potassium and ammonium nitrates. Under high pressures these nitrates undergo a transition and the crystals in the high-pressure phase are much smaller in size than in the low-pressure phase (figure 3). The crystals in the low-pressure regions have a preferred orientation with their longest directions radial to the center of the high-pressure cell (figure 4); this is also the direction of the pressure gradient. By changing pressure, a growing crystal front that has the appearance of a liquid interface can be produced.

#### 4.11. Optical Observation of Pressure - Induced Transitions in Polymers

J. Powers, F. Quinn,

Macromolecules Synthesis & Structure Section

R. Neuman, Dielectrics Section

A wide variety of polymers display an abrupt decrease in thickness and change in



morphological appearance with slight increase in pressure when viewed by light transmitted through a diamond pressure cell. At present, a phenomenological description is employed in interpretation. X-ray diffraction and infrared spectroscopic data will be taken and should lead to an explanation in terms of molecular theories.

#### 4.12. Crystallization of Noble Gases

G. L. Pollack, Crystal Growth Section

Dissolved nitric oxide in solid krypton was studied spectroscopically. Thermal etching of argon crystals was observed, and a series of experiments to correlate the observed grain boundaries with growth conditions was begun. Microscopic observation of whisker growth of argon was also started. A thin-cell cryostat for the X-ray study of these crystals was designed and built.

#### 4.13. A Study toward the Growth of Single Crystals

L. H. Bolz, Crystallography Section

H. P. Broida, NBS Senior Research Fellow

A special dewar for the growth and examination (by the X-ray diffraction method) of argon crystals was built and used in a study published by L. H. Bolz, H. P. Broida and H. S. Peiser (1962). It was found that the clear solid formed by slow cooling of liquid argon was polycrystalline, but the grain size of individual crystallites ranged up to 4 mm. The larger grains were produced by slower cooling rates. These results encourage the view that large crystals of argon can be grown.

#### 4.14. Study of Crystal Growth in Vapor Snakes

G. L. Pollack, F. Ordway, Crystal Growth Section

and H. P. Broida, Senior Research Fellow

Vapor snakes are hollow crystal cylinders filled with vapor which sometimes form in a closed vessel filled with liquid near the triple point when heat is slowly extracted.

Vapor-snake growth in argon has been observed before the reporting period and measurements of the dimensions and growth rates of vapor snakes were made from motion-picture films. A theory treating the growth as an essentially adiabatic process gave estimates of the ratio of diameter to thickness of the solid sheath in reasonable agreement with the observations, (Pollack and Broida, 1963). A discussion of the process in terms of relations between undercooling and growth rate was found to explain qualitatively the mode of formation and growth, and to state necessary conditions for the phenomenon. Preliminary designs were sketched for an apparatus in which vapor snakes can be produced with all variables under direct control.

#### 4.15. Growth Kinetics of Crystal Whiskers by Field-Emission Techniques

S. C. Hardy and R. L. Parker

Metal Physics Section

The purpose of this project is to study, by field-emission techniques, the vapor phase growth kinetics of metal crystal whiskers.

A paper on this subject has recently been published (Parker and Hardy, 1962). The abstract of this paper reads as follows:

"Using the method originated by Gomer, we have studied the growth kinetics of potassium whiskers, as they grow from the vapor phase in an electron field emission tube. To the best of our knowledge, this represents the first use of an alkali metal as a field emitter.

The results for potassium whiskers show some features similar to those previously found for mercury, and some new features. The former include positive exponential growth, and the attainment of terminal lengths. New features include the absence, usually, of symmetric emission patterns, a very low activation energy for surface self-diffusion, the fact that the whiskers cannot be pulled off but instead appear to shorten gradually if the field is raised, and finally an interesting sensitivity of the growth processes to illumination of the whiskers with visible light."

Experimental work since this publication has concentrated on the study of the effects of sputtering (ion bombardment) on the observations of potassium whisker growth, and on field-emission tubes designed to permit simultaneous optical and field-emission measurements.

This work has been slow due to experimental difficulties arising from the use of potassium (effects on fluorescent screens and persistent emission patterns from substrates). A second ultra high vacuum system, to permit faster tube preparation, was designed, constructed, and put into operation. The field-emission dark-room was enlarged. Preliminary planning and calculations on the use of W emitters to study the nucleation of K and Hg whiskers were performed - they indicate that both qualitative and quantitative observations of the heterogeneous nucleation process can be made in these systems.

#### 4.16. Kinetics of Whisker Evaporation

R. L. Parker and R. L. Anderson

Metal Physics Section

The purpose of this project is to investigate the role of crystal edges as step sources in evaporation.

Several hundred photographs have been taken of potassium whiskers during both their growth and evaporation from the vapor phase. The evaporation experiments have covered a range of pressure ratios  $P/P_0^*$  from 1.0 to 0.05. Over this range of pressure ratios the whiskers evaporate from the tip only, in rather the reverse process of growth. Hence there exists a considerable undersaturation for the nucleation of evaporation steps on potassium whisker edges, contrary to a theory by Hirth and Pound but in agreement with a recent prediction by Cabrera. More precise nucleation calculations for this case are being made; also, there appears to be no previous solution to the surface diffusion equation in this case and this is being studied.

#### 4.17. Theoretical Studies in Whisker Crystal Growth

R. E. Howard and R. L. Parker

Metal Physics Section

Previous treatments of whisker growth from the vapor phase have assumed a steady-state diffusion process, i.e. that in the surface diffusion equation,  $\delta C / \delta t = D \delta^2 C / \delta x^2 - C / \tau + N$ ,  $\delta C / \delta t$  is zero.

This, however, is clearly not a good assumption in the field-emission microscope observations of whisker growth. Several methods for treating this moving boundary problem have been examined and currently an integral equation incorporating the boundary conditions has been obtained. Asymptotic solutions for simple cases are being looked for; it is expected that complete solutions of this non-linear equation will require numerical computation; in this assistance from the Applied Mathematics Division is being received.

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\* Actual pressure divided by equilibrium vapor pressure.

#### 4.18. Freezing Behavior on Adsorbing Surfaces

G. S. Ross, L. J. Frolen and C. Gray

Pure Substances Section

When the purity of a sample of isopropyl alcohol was measured by the cryoscopic method, two crystalline forms were observed. The presence of a very fine, white crystalline residue was observed in the transferring vessels. After this powder was removed by centrifuging only the high melting form was obtained; if the powder was present either form could be obtained primarily depending upon the rate of cooling.

In order to obtain further information concerning the role of adsorbing surfaces on crystallization the following study was instigated. The freezing and melting behavior of water and benzene adsorbed on silica gel and bone char was examined using the technique of differential thermal analysis. For these experiments the difference in temperature between the blank and the sample was plotted against the bath temperature on an x-y recorder. When the sample froze the energy liberated produced a difference in temperature between the blank and the sample which was displayed as a peak on the x-y plot. A previous study [J. A. Patrick and W. A. Kemper, J. Phys. Chem. 42, 369 (1938)] using a simple calorimeter had been largely unsuccessful.

In the initial experiments for water adsorbed on silica gel, no free water was visible. Two transitions were observed, one at  $-11^{\circ}\text{C}$  and one at  $-37^{\circ}\text{C}$ . Repetitions of the freezing-melting cycle produced a high, sharp peak at  $-5^{\circ}\text{C}$  accompanied by a noticeable change in physical characteristics as would be explained by a wetness above this temperature. The peak at  $-11^{\circ}\text{C}$  decreased and finally disappeared as the height of the peak at  $-5^{\circ}\text{C}$  increased. This peak ( $-11^{\circ}\text{C}$ ) is undoubtedly due to capillary-held water and the freezing process tends to break down the internal gel structure rendering the gel visibly wet. The peak at  $-37^{\circ}\text{C}$  is unchanged and is due to surface adsorbed water.

Water absorbed on bone char results in a peak at  $-39.6^{\circ}\text{C}$  which is roughly the same size and shape as the peak observed at  $-37^{\circ}\text{C}$  for silica gel and is probably due to surface-adsorbed water. One additional peak, slightly below the freezing point of water, was observed but its direction was reversed. This behavior is as yet unexplained. Cooling to  $77^{\circ}\text{K}$  produced no peak corresponding to capillary-held water.

The experiments on benzene are still in progress at this time, but their results appear to be similar to those on water.

When silica gel is treated by freezing adsorbed water thereby breaking up the internal capillaries, much sharper separations are obtained. This is thought to be due to the lack of diffusion-controlled migration on the gel.

Further studies on heterogeneous and homogeneous nucleation are being contemplated to explain further the freezing behavior of capillary-held materials.

#### 4.19. Growth of Oxide Films on Aluminum Single-Crystal Surfaces

T. H. Orem, Metal Reactions Section

The principal purpose of this project is to obtain a better understanding of the corrosion process and its relation to crystal structure and atomic surface arrangements. The reason for referring to this project in this report is the considerable skill developed in the melt growth and repeated crystallization by a Bridgman technique of large pure aluminum crystals.

A paper on the wider subject was given at the July 1962 Gordon Research Conference on Corrosion. In studying the relationship between the oxide film and the aluminum single-crystal surface, it was found that certain surface markings appear on the oxide film that are always characterized by having their boundaries parallel to faces of close-packed planes in the underlying metal surfaces.



The unequivocal observation of growth twinning in aluminum is another result arising from this work (see Orem, 1963).

#### 4.20. A Spontaneous Martensitic Transformation

R. P. Reed, Properties of Materials Section

The abstract of a recent paper (Reed, 1962) reads as follows:

"On cooling, 18% Cr, 8% Ni steels transform martensitically to two products ( $\epsilon$  and  $\alpha'$ ). Sheets representing either  $\epsilon$  (h.c.p.) or stacking fault clusters have been observed to form prior to the formation of  $\alpha'$  (b.c.c.). Photographic sequences demonstrating the formation of  $\alpha'$  from these sheets are included. Transformation characteristics of both  $\epsilon$  and  $\alpha'$  are discussed.

"The morphology of the  $\alpha'$  has been determined. It was found that the  $\alpha'$  formed as long, narrow plates and that these plates were bounded by  $\{111\}$  sheets. The long direction of the plates was parallel to or nearly parallel to  $\langle 110 \rangle$ . If they were parallel to  $\langle 110 \rangle$  then the plates had 225 habit planes. If they deviated from  $\langle 110 \rangle$  then the habit plane was not  $\{225\}$ ; possible alternate habit planes are plotted.

"In addition, the  $\{111\}$  habit plane was observed."

#### 4.21. Radio Materials Synthesis

P. M. Gruzensky, C. Jefferson, and, in part, D. R. Winder

Radio & Microwave Materials Section

Boulder Laboratories

The Radio Materials Section has a project on Radio Materials Synthesis whose primary objective is to synthesize chemical compounds whose composition and structure are of primary interest because of their radio and microwave properties and to investigate fundamental aspects of such syntheses as have a bearing on the chemical, magnetic, dielectric, or conductivity properties of these materials. Well characterized specimens of adequate purity or properly controlled impurity as well as composition and structure are essential to safeguard the meaningfulness of magnetic, dielectric, and conductivity measurements for a program on Radio Standards. Only materials of adequate characterization which are not readily available elsewhere are included in this program.

Primary efforts during fiscal year 1962 have been devoted to the development of a process for growing single crystals of anhydrous sulfates of the transition metals, principally copper sulfate and cobalt sulfate. A solvent system consisting of ammonium sulfate and sulfuric acid has shown considerable promise, yielding anhydrous copper sulfate single crystals with edge dimensions up to 3 mm. To our knowledge, these are the first anhydrous copper sulfate single crystals that have been produced in this country. Single crystals of these compounds are of interest because of their antiferromagnetic properties at low temperatures. In addition, the same system has proved to be an excellent solvent for anhydrous zinc sulfate. Preliminary experiments indicate that it may be possible to grow sizable single crystals of zinc sulfate doped with a wide variety of paramagnetic ions.

Tutton salt, a hydrated form of zinc ammonium sulfate, has been used in the past as a host crystal for paramagnetic ions in the study of crystalline electrostatic fields. During the fiscal year, several Tutton-salt specimens, doped with divalent and tetravalent vanadium, were prepared. Incorporation of the divalent form into the lattice required some special techniques to prevent oxidation.

A series of nickel ferrite toroid specimens, with intentional additions of zinc, cobalt, and manganese in trace amounts, were prepared for magnetostriction studies. Specimens of nickel zinc ferrite, similar in composition to a commercial material which shows an anomalous resonance peak, were also prepared.

Samples of high-purity nickel metal powder have been melted by induction heating to produce massive metal suitable for machining to specimens of proper geometry for magnetic measurements. Analysis of this material by emission spectroscopy indicates the presence of total metallic impurities in the range of 50 to 100 parts per million.

During the last quarter of the fiscal year a program was initiated to investigate the chemical and magnetic properties of magnetic ilmenites. Early results indicate that ilmenites can be prepared with moderate magnetic moments at 25°C.

Efforts will continue to establish the optimum conditions for growth of sizable single crystals of anhydrous transition metal sulfates. It is also anticipated that the synthesis of calcite single crystals will be given consideration, as well as a continuation of magnetic ceramic oxide materials preparation for high power spin-wave studies as well as other ferrite investigations.

Nickel whiskers of up to 2 cm in length have been successfully grown for studies in dimensionality in magnetization. These whiskers contrast with 2 mm length whiskers previously reported in the literature by others.

## 5. CRYSTAL CHARACTERIZATION

### 5.1. Thermal and Chemical Etching of Dislocations

A. W. Ruff, Jr.,  
Metal Physics Section

The purpose of this project is to obtain a better understanding of the relationship between etch pits and dislocations in metal crystals.

As described in a recent paper on this subject, (A. W. Ruff, Jr., 1962) thin copper single-crystal foils were deformed so as to introduce fresh dislocations, and then etched in one of several solutions which had been developed to reveal dislocations intersecting the (111) surface. Then transmission electron microscopy permitted direct study of both etch pits and dislocations. The results indicated that dislocations vary in their ability to nucleate etching, and that other crystal defects can be effective nucleation sites.

A further study now underway involves thermal etch-pitting (by evaporation) on  $\{0001\}$  surfaces of zinc crystals, in ultra-high vacua. The interest lies in comparing observed and predicted critical under-saturations for nucleation of pits at dislocations, and on the effects of impurities. Some preliminary experiments have been started showing by surface two-beam interference microscopy quite regular pit morphologies.

### 5.2. The Effect of Point Defects on Dynamic Properties of Crystals

J. B. Wachtman, Jr.  
Physical Properties Section

Elastic and electrical properties are being studied as a function of temperature and frequency, and the results are interpreted in terms of chemical impurities and related point defects. Papers on the relaxation processes associated with CaO in ThO<sub>2</sub> and with nonstoichiometry in TiO<sub>2</sub> (rutile) are in press. A program of measurements on magnesium oxide, doped with various impurities is in progress. The only relevant publication which appeared during this reporting period is a theoretical paper on symmetry conditions for internal friction (Wachtman and Peiser, 1962). The influence of oscillatory homogeneous strain is considered on the jump rate of unclustered point defects between sites that are symmetry related in the unstrained crystal. Only strains that can destroy the operative symmetry can, it is held, bias the jump rate and hence cause the type of internal friction that is here considered. A rather exhaustive study of the influence of strains in any given orientation on crystals of any given structure is therefore being attempted.

### 5.3. Further Studies of Crystal Defects in the Inorganic Solids Division\*

F. Ordway, Crystal Growth Section

In search of experimental data on the mobility of defects an attempt is being made to determine the activation energy for diffusion of aluminum in rutile. Most of the specimens and about half the necessary diffusion runs have been made.

Several crystals with the rutile structure were explored for possible use in the study of dislocation arrays by transmission electron microscopy. Crystals of tellurite,  $\text{TeO}_2$ , grown by vapor deposition, were too thick. Cleavage of the fluorides,  $\text{CoF}_2$  and  $\text{MgF}_2$ , yielded promising specimens. Chemical thinning by strong alkali hydroxide solutions was found promising, and attempts to develop a dependable procedure for routine preparation of electron-microscope specimens were begun. A supply of  $\text{CoF}_2$  powder was prepared for the growth of additional crystals.

It was found possible to reveal dislocations in the oxides,  $\text{Cr}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , by etching with fused alkali hydroxide and constant-boiling hydrochloric acid respectively. Phosphoric acid was found to be a chemical polish for  $\text{Cr}_2\text{O}_3$ .

Tests of the divergent-beam and reflection techniques for study of crystal texture by X-rays were made to find suitable conditions of specimen preparation and exposure. A high-intensity rotating-anode X-ray generator was installed and put into operation, to speed the production of orientation and texture patterns.

### 5.4. Evaluation of Radiation Damage by Solution Calorimetry\*

E. J. Prosen, Physical Chemistry Division  
and M. V. Kilday, Thermochemistry Section

An adiabatic solution calorimeter has been designed to determine the difference in heats of solution of irradiated and non-irradiated crystals. In contrast with differential thermal analysis (DTA), the calorimetric data will yield values of the total "stored energy" in the crystals.

Adiabatic shielding is used so that high precision may be obtained even for sparingly soluble materials, for which elevated temperatures will be required. The calorimetric vessel is constructed with an inner liner of platinum, so that solvents such as  $\text{HF}(\text{aq.})$  may be used.

Upon completing of the apparatus, in the spring of 1963, our first task will be a determination of the irradiation damage or stored energy in samples of quartz for the Atomic Energy Commission. These measurements may be followed by other similar measurements for the AEC. We also plan to make measurements on the effect of particle size on the heat of solution.

Bomb combustion techniques have also been used in this laboratory for many years to determine the total "stored energy" in the samples of graphite and diamond. These techniques could also be applied to other materials for which a suitable combustion reaction is available.

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\* These studies were made with partial support from the Atomic Energy Commission.



## 5.5. Studies in Solid State Theory

A. H. Kahn, Solid State Physics Section

a.) A calculation of the electronic energy band structure of rutile ( $\text{TiO}_2$ ) is related to the electronic transport measurements (5.15) and to reflectivity measurements carried out at RCA. This calculation is ready for the computer.

b.) A computation of the g-factors of the  $\text{V}^{4+}$  ion in rutile) is an important test of the crystal field theory, which is the basis of laser and maser applications. The expressions derived by Van Vleck do not seem to fit.

S. J. Glass, Solid State Physics Section

c.) It is well known that spinwaves cannot be represented either by bosons or by fermions. An intermediate description is explored in cooperation with Professor Tanaka (Catholic University).

d.) An investigation dealing with an expression for the melting curve (P,T) is shortly to be ready for publication.

## 5.6. Improvements in the Measurement of Refractive Indices of Microscopic Crystals

C. P. Saylor, Analytical and Inorganic Chemistry Division

When the immersion methods for measuring the refractive indices of crystals are employed, an accuracy within  $\pm 0.001$  is ordinarily looked upon as good and within  $\pm 0.000,5$  as exceptionally good. By phase- or interference-contrast procedures, however, a difference in index between a crystal 5 microns in diameter, and an immersion fluid can be perceived when it is as small as  $\pm 0.000,05$ . The preparation of liquids can be controlled and their indices measured to an even higher accuracy.

The problem of translating such precision to the determination of the index of refraction of a crystal involves the steps of orienting the crystal, verifying its orientation, identifying the polarization direction, controlling the index of the liquid, while observing the mismatch, and measuring the index of the liquid. Actually by employing two readings, one when the index of the liquid is just perceptibly above and the other when it is just perceptibly below that of the crystal - and then averaging - a precision of refractive-index determination within about  $\pm 0.000,015$  has been demonstrated to be attainable. Careful analysis fails to reveal a reason to suspect a bias in these results, so that it may be inferred that the accuracy is the same. Notable novelties in the procedures developed involve the methods of orienting and determining the orientation of the crystal, controlling the index of the liquid, and the measurement of the refraction index of the liquid. In particular a microscope differential refractometer has been developed with which the refractive index of the liquid can be measured to within  $\pm 0.000,01$  without removing it from the slide. The greatest experimental difficulty is that of adequate temperature control.

## 5.7. Optical Property Studies in the Inorganic Solids Division

R. W. Dickson

Physical Properties Section

A ruby laser has been set up and it is planned to use the laser beam in a study of the clustering of chromium atoms in ruby.

## 5.8. Optical Property Studies in the Solid State Physics Section\*

L. H. Grabner, R. F. Blunt, H. Frederikse, and J. Becker

a.) Semiconductors: During the last few months the 2-6 compounds (in particular cadmium telluride, CdTe) have become the center of attention. The aim is to study absorption, photoconductivity and luminescence simultaneously. Especially important is the possibility of stimulated electroluminescence (laser) similar to the effect observed in gallium arsenide, GaAs, (at the General Electric Laboratories, IBM and Lincoln Laboratories, October 1962). Efforts are concentrated on preparing p-n barriers.

b.) Defect Studies: Defects and impurities in ionic crystals are investigated using optical tools. Measurements of the absorption spectrum are performed on several systems. Magnesium-aluminum spinel doped with cobalt is presently being studied. These spectra will indicate if the Co is situated in tetrahedral or in octahedral sites. Comparison with crystal field theory will be made. Other systems under consideration are:

TiO <sub>2</sub> (:Mo)	TiO <sub>2</sub> (:W)	
spinel (:Mn)	LiF (:Ti)	MgO (:Ti)
spinel (:Cr)	MgO (:Ni)	MnF <sub>2</sub> (:Sm) etc.

Other aspects to be studied are: pair formation [see Linz and Newham, Phys. Rev. 123, 500 (1961)], defect structure (reduced TiO<sub>2</sub>, SrTiO<sub>3</sub>), luminescence lines under uniaxial stress, etc.

Correlation with electron spin resonance results (see Section 5.19) is one of the major aspects of this project.

## 5.9. Activity of the Spectrochemistry Section

B. F. Scribner

In the Spectrochemistry Section increasing attention is being given to extending the sensitivity and the precision of spectrographic methods of analysis to meet the severe problem in the analysis of present day materials. Of particular interest are the improvement of excitation sources and the application of higher spectral resolution; both of these are aimed at increasing the spectral line-to-background ratio with resulting gain in sensitivity. One of the promising possibilities for spectral excitation is the application of the laser (optical maser) and particular attention is now being given to this source. In the proposed application the laser serves to produce a short duration pulse (100 microseconds) of high-energy coherent light which is focussed on a sample surface by means of a microscope. The energy in the beam is sufficient to volatilize a portion of the sample as a jet which rises between two charged electrodes. The vapor jet serves to trigger a capacitor discharge between the electrodes and this excites the vapor to produce light, the spectrum of which is photographed.

Although much needs to be learned of the utility of the laser source, its potential advantages may be listed as follows:-

a.) It excites a very small portion of sample with a single pulse. An area 10 to 50 microns in diameter is involved at present but this may possibly be reduced to a smaller area to provide a micro-probe source for analysis of very small samples such as portions of a specific face of a crystal or of segregates or inclusions in samples.

b.) The sample is excited under conditions which should result in a minimum possibility of contamination. This offers a good possibility for the analysis of high purity materials if the sensitivity of detection proves to be adequate.

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\* These studies were made with partial support from the Office of Naval Research.

HCl<sup>35</sup>-Ar (1:1000) matrix

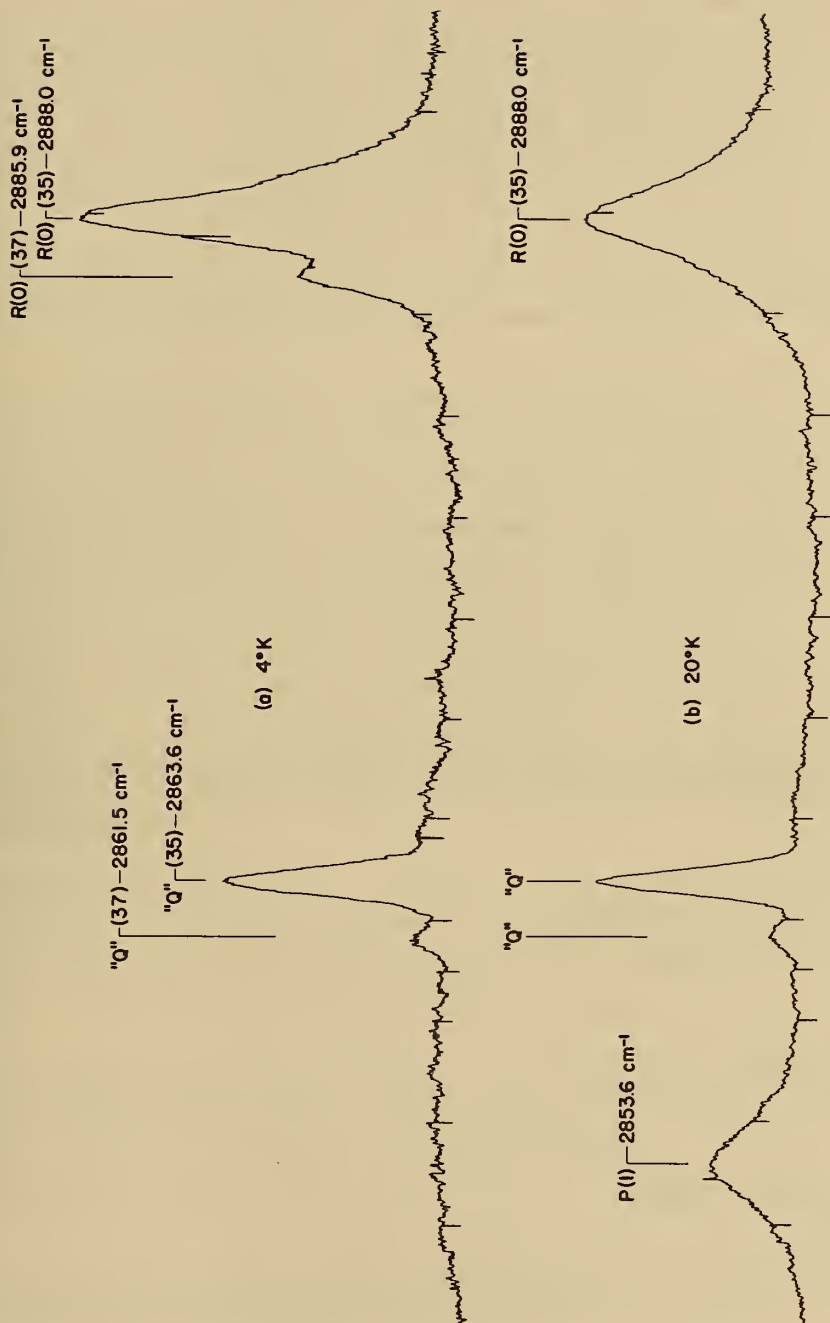


Figure 5. Matrix-Isolation Spectra of HCl in Argon (1:1000) at 4° and 20°K in the Region of the Fundamental.



d.) Almost all elements in the periodic system may be excited simultaneously, and their spectra observed. The exceptions are the gaseous elements, but these may be capable of observation under special conditions.

Recently a bread-board assembly of a laser excitation source was observed in operation. Samples of zinc, zirconium, agate, and glass from our laboratory were excited by the laser and the resultant spectra and pit patterns produced by the laser were studied. The observations appeared sufficiently promising to warrant proceeding with the procurement of equipment to permit detailed studies to be made in our laboratory. Accordingly, the equipment was ordered and will be built by the manufacturer after consultations with our laboratory on details of the design especially relative to the sample mounting-mechanism and the facility to choose a vacuum or a noble-gas atmosphere. The equipment is expected to be delivered in about 3 months, after which its characteristics and applications will be investigated.

In addition to its potential applications to elemental analysis, the laser may also be effective for exciting fluorescence spectra and Raman spectra, particularly of small crystals. These possibilities may be investigated later.

#### 5.10. Crystal-Field Studies by Matrix Spectroscopy

D. E. Mann, Molecular Spectroscopy Section

The principal object of this research is the investigation of crystal field effects through their influence on the rotation-vibration spectra of simple entrapped molecules. We have recently shown that hydrogen and deuterium chloride molecules isolated in solid argon or krypton matrices are capable of molecular rotation over the range 4-20°K (Schoen, Mann, Knobler, and White, 1962). Their infrared spectra are clearly perturbed by environmental influences in several different ways. First, the vibrational band centers are shifted slightly to the red. Second, the lowest rotational spacing and hence the effective moment of inertia of the trapped species is appreciably affected. Third, the rotational lines for higher levels are either abnormally spaced or absent altogether. Fourth, the spectra of isotopically related species suffer quite different degrees of perturbation in the same environment. Fifth, under certain experimental conditions the spectra of the same species in a non-rotating state also appear. While a complete and detailed understanding of these effects is not yet at hand and must await further study, it is already quite clear that their interpretation will convey much useful information about the nature and structure of the host matrix.

A typical spectrum is shown in figure 5 where R(0) and P(1) refer to the rotational transitions, and Q indicates absorption by non-rotating species.

#### 5.11. Soft X-Ray Spectroscopy of the Solid State

R. D. Deslattes, Crystal Chemistry Section

Activities are planned in two areas: (1) Study of certain aspects of X-ray spectra, and (2) application of X-ray techniques to the study of imperfections in crystals.

Work began on this project in September 1962. Since that time designs for apparatus required for both activities have been largely completed. Provisional assembly of a vacuum two-crystal spectrometer is underway.

Initial application of the vacuum instrument will be to obtain comparable K-series spectra of gaseous and solid neon, metallic sodium and sodium fluoride. It is planned to apply a second (air) two-crystal spectrometer to certain Borrmann-effect and rocking-curve studies with a view to their use in the characterization of highly perfect crystals.

## 5.12. The Precise Measurement of X-Ray Diffraction Patterns of Powdered Crystals

H. E. Swanson, Crystallography Section

Standard X-ray powder diffraction patterns of pure and well characterized inorganic solids are being produced under partial support from the Joint Committee for Chemical Analysis by X-Ray Diffraction, American Society for Testing and Materials. The aim is to obtain very accurate X-ray diffraction data that can be used for comparison standards in identifying crystalline materials of unknown composition. It has not been possible to obtain an adequate number of pure and well crystallized samples from commercial sources and a chemist has been employed to synthesize, purify, and crystallize additional materials. Information about the preparation, chemical purity, and crystallinity of these samples, together with optical and X-ray diffraction data, are included in bi-monthly reports and later consolidated in NBS Monographs, twelve of which have been published to date. The last one of these is listed in the references (Swanson et al., 1962). During the past six months, fifteen compounds have been processed and the results have been published in NBS Report 7521, 7592, and 7741, the contents of which will be published in future NBS Monographs.

Related to the above activity is a project on the precision measurement of lattice constants using powder samples. A special high-angle, focusing, back-reflection plate camera has been built which includes features that permit control of specimen temperature to 0.01°C and accurate measurement of the specimen-to-plate distance. Measurements of the lattice constants of cadmium oxide and gold have been completed and the results are being compared with those obtained at the National Physical Laboratory in England. The precision of the measurements made with the new camera is expected to be sufficient to permit small departures to be determined in the lattice constants due to vacancies or impurities.

## 5.13. High-Voltage Laue X-Ray Photography

B. Paretzkin, H. S. Peiser and E. P. Levine

Crystal Chemistry Section

A paper on this subject was presented to the Eleventh Annual Denver Conference on Advances in X-Ray Analysis and will be published in the proceedings of that Conference (Peiser and Levine, 1963).

The abstract of this paper reads as follows:

"Large single crystals can be examined by conventional X-ray diffraction procedures only at their surface or by destructive sectioning. Within the limitations inherent in polychromatic X-ray photography, high voltage Laue pictures are shown to give some information on the internal quality of large crystals.

"Asterism in conventional Laue photographs is contrasted with streaks due to geometric effects in Laue patterns of large crystals. Detail within the streaks reveals sub-grain structure. A primary extinction effect can be used as striking proof of good crystals being capable of scattering coherently over large distances."

Since that lecture was delivered a high-voltage (up to 150kv) fine-focus X-ray generator and a slit assembly for producing parallel X-rays have been successfully installed.

A comparison study has been started of the perfection of aluminum crystals differing in method of growth and of ammonium dihydrogen phosphate crystals with varying degrees of chromium contamination (see Section 4.5).



5.14. Precision Measurement of the Fundamental  
Electrical Properties of Semiconductor Crystals

J. C. French and L. J. Swartzendruber  
Electron Devices Section

This project was established late in December 1962 to conduct research into the methods of measuring the fundamental electrical properties of crystalline semiconductor materials used in electron devices, in support of the development of improved theory and techniques of measurement, and of standards for the measurement of appropriate properties. The principal short-term objectives will be the establishment of the experimental equipment required for the measurement of the homogeneity of the resistivity of germanium and silicon single crystals by a traveling probe method, and the determination of the uniformity of resistivity in crystals which are grown by various methods or which are made to be more uniform by neutron irradiation. This will require the development of sample preparation techniques and the study of the effects on probe measurements of the semiconductor surface conditions, needle force, and other factors. It is also planned that the feasibility of other methods of determining homogeneity of resistivity will be considered.

The importance in itself of this new project for the general aims of the NBS/ARPA program can be readily appreciated, because no physical property is more widely used for characterization of crystals than resistivity, yet its measurement is subject to experimental imprecisions and interpretative ambiguities which one can confidently hope to reduce by careful experimentation such as is commonly applied in standards measurement problems.

At the same time the new project fits in remarkably well with the existing semiconductor device studies, under the leadership of J. C. French, the general objectives of which are the investigation of semiconductor devices and the semiconductor materials used, their specification, evaluation, and the development and standardization of methods of analysis.

This previously existing work has received partial support from the Air Force, Cambridge Research Laboratories and is divided into several tasks:-

a.) Establishment of device parameter measurement equipment and techniques: Facilities for measurement of a variety of characteristics of semiconductor devices have been established. Examples are (1) voltage-current characteristics, (2) swept or pulsed families of characteristic curves, (3) small signal parameters at a variety of frequencies, (4) thermal resistance and (5) capacitance-voltage characteristics of junctions.

b.) Provision of measurement and advisory services to other groups and organizations: This has been primarily the determination of electrical characteristics, structural materials, and fabrication techniques (including determination of junction types, etc.) of devices for another agency.

c.) Participation in the standardization activities of the Joint Electron Device Engineering Councils, American Standards Association, and American Society for Testing Materials: This function covers attendance at committee meetings, reports on our progress in related work, and general liaison with the industries.

d.) Study of the characteristics and physical processes of second breakdown in transistors: This is research into an important but unexplained phenomenon of transistor action (Schafft and French, 1962).

e.) Improvement and standardization of the characterization of device semiconductor materials: This task continues in parallel with the new work. It will cover (1) the development of a new one-probe technique for measuring bulk resistivity of thin semiconductor single-crystals, (2) microwave techniques for bulk resistivity measurements, and (3) the application to industry standardization of the results of the research conducted under the new project.



Brief mention should also be made of the equally closely related electroluminescence and contact studies (project leader G. G. Harman) to develop methods of measuring contact phenomena, electroluminescent and thermoelectric properties of silicon carbide and other semiconducting crystals.

Two recent publications in these fields are included in the reference list (Harman and Higier, 1962; Harman, Higier and Meyer 1963).

#### 5.15 Electronic Transport\*

H. Frederikse and J. Becker  
Solid State Physics Section

The main topic in electron transport is the conduction mechanism in rutile ( $\text{TiO}_2$ ).

a.) Measurements are being made of the conductivity ( $\sigma$ ) and the Hall effect ( $R_H$ ). The emphasis is on the very low temperature end of the scale. There is an indication that conduction in impurity levels or impurity bands is predominant below 4°K. Samples with different amounts of aluminum, different reductions and different Frenkel defect concentrations are investigated. The purpose of this research is to obtain information about the nature of the defects in  $\text{TiO}_2$ .

b.) Measurements of  $\sigma$  and  $R_H$  in the range 10-300°K are performed on oriented samples to study the anisotropy of the electronic band structure (see also Section 5.5-a).

c.) Thermoelectric power studies below room temperature indicate a large phonon-drag effect. The main problem is to separate this effect from the possible temperature dependence of the effective mass.

#### 5.16. Hall-Effect Measurements

S. Rubin, Engineering Electronics Section

The objectives of this project are the establishment of standardized measuring methods and terminology for Hall-effect generators and related Hall-effect devices.

This project was begun early in 1962 with the acquisition of a suitable magnet, a survey of the literature, the development of a transistorized nuclear-magnetic-resonance gauss meter, and the development of small probes for precise measurement of high-intensity fields (2 to 3 tesla) in small gaps (0.25 in). Other work has had to do with standards for devices, including color codes and figures of merit, and methods of measurement of device properties.

#### 5.17. Dielectric Constant and Losses\*\*

J. H. Wasilik, Solid State Physics Section

Preparations are being made to explore the possibility of a dielectric loss due to excitons in  $\text{Cu}_2\text{O}$ . The real part of the dielectric constant will also be measured. Due to the large size of the exciton, especially in the higher states ( $d = 100 \text{ \AA}$  for  $n = 2$  and  $2500 \text{ \AA}$  for  $n = 10$ ) [Gross, J. Phys. Chem. Solids 8, 173 (1959)], the contribution to  $\epsilon'$  should be large. Exploration will take place at frequencies up to 10 Mc, temperatures down to He-temperature and light energies 1.9 - 2.3 ev.

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\*This work was carried out with partial support from the Office of Naval Research.

\*\*This work was supported by the Atomic Energy Commission.

## 5.18. Dielectrimetric Cryoscopy

G. S. Ross and L. J. Frolen

Pure Substances Section

Cryoscopic techniques constitute one of the more accurate methods of purity analysis. This determination of freezing-point depression is usually achieved by one of three techniques: (1) dilatometric, (2) calorimetric, or (3) thermometric (time-temperature). While differing greatly in detail, the success of each method is dependent upon accurate determination of a series of temperature (T) and fraction-melted (F) values as a sample undergoes freezing or melting. As practiced, the precision of the analysis is dependent upon the quantity of the sample which is used. This does not appear to be a serious limitation of another process currently being developed. This process, called dielectrimetric cryoscopy, like the other methods, depends upon an accurate measurement of T versus F. However, F is determined by correlation of the change in dielectric constant which is an intensive property. The temperature which is measured is the temperature of the cryometric vessel, and the accuracy of this measurement is likewise not dependent upon the quantity of sample; indeed it may be advantageous to use small samples. While the apparatus and techniques now used can be improved, the general utility of the method appears to be proven by experiments conducted to date.

In practice the sample (solid) completely fills the space between two capacitance plates. The outer, ground-potential electrode has the form of a cylinder with one closed end and serves as the container for the sample. When melting occurs, excess sample resulting from the increase in volume flows over the top of the inner electrode. This cell and a precision, variable capacitor comprise two arms of a four-armed capacitance-inductance bridge. In these analyses it is assumed that the materials being tested, having undergone a rather rigorous purification, contain only impurities which are similar in dielectric properties to the bulk sample. If this is so, then any change in dielectric constant is almost exclusively the result of the change in density and orientation of the major constituent as the fusion takes place.

These melting experiments take place in 6 to 24 hours. Shields are maintained at a temperature just above the melting point of the sample. The heating pattern is such that the sample melts from the outside, progressively producing a thicker cylinder of liquid as the fusion proceeds. There are large end-effects in the cell and each solid-liquid distribution produces varying results, making mathematical analysis of the system extremely difficult. However, for the purposes of this work, it was only necessary that the change in capacitance represent a reasonably linear dependence with the fraction melted. If this dependence exists, then a plot of impedance (or phase angle) versus temperature should be equivalent to plotting F versus temperature, resulting in a hyperbolic curve similar to those obtained by time-temperature methods. Assuming the capacitance change is a linear function of the fraction melted, then the ratio of the change at any time to the total capacitance change during the entire process should correspond to the fraction melted, and the plot of  $1/F$  versus  $T_x$ , the experimental temperature corresponding to any particular  $1/F$  value, should result in a straight line. The equation for the relationship between impurity and the depression of the freezing point is:  $T_x = T_{f_0} - N_2(RT_{f_0}^2 / \Delta T_f) (1/F)$ .

Experiments were run using three types of organic materials: (1) non-polar, non-polarizable, (2) polar, and (3) non-polar but readily polarizable. The specific samples used were: (1) naphthalene, (2)  $\beta$ -methylnaphthalene and nitrobenzene, and (3) p-dichlorobenzene. For each material a plot of  $1/F$  versus T was linear over the  $1/F$  range of 1.5 to 6.0. The calculated  $T_f$  and  $T_{f_0}$  values corresponding respectively to  $1/F = 1$  and  $1/F = 0$  of at least six experiments for each sample with the exception of nitrobenzene showed standard deviations which were smaller than those obtained by time-temperature methods on samples of comparable purity. Preliminary work indicates that nitrobenzene will show the same degree of precision, but work has not yet been completed upon this compound. The sample of naphthalene used gave a calculated purity of 99.989 mole percent with an estimated probable error 0.001 mole percent. This and similar values for the other materials have not been substantiated by other methods of analysis, but comparative time-temperature analyses will be made. If these results are substantiated by alternate procedures, and this is almost



assured by the linear dependence which exists between  $1/F$  and  $T$ , the method will have been shown to be applicable for the analysis of a large percentage of organic materials. The basic limitation of the method would appear to be in its failure to deal adequately with materials which have an appreciable electrical conductivity.

One obvious use for such a system other than as a method of purity analysis is the use of a modified cell as a secondary temperature standard. Exploratory work along these lines in addition to studies in heterogeneous equilibria and in heterogeneous and homogeneous nucleation and crystal growth are planned using the same basic dielectric techniques.

#### 5.19. Magnetic-Resonance Studies in the Solid State Physics Section

T. P. Chang and A. Kahn

a.) Electron spin resonance: This project focuses its attention at the moment on molybdenum-doped  $TiO_2$ . Using the sample of rutile as its own cavity, large  $Q$  values (20,000) are obtained at 77 and 4°K. With the magnetic field in an arbitrary direction 117 well-resolved lines are observed. These lines are due to the Mo and Ti fine-, hyperfine-, and superhyperfine-structure. Important conclusions concerning the crystal field and overlap can be derived from the results.

Other systems under investigation are reduced  $TiO_2$ ,  $LiF(:Ti)$  and  $spinel(:Co)$ .

R. A. Forman

b.) Quadrupole resonance\*: The Na- and N-nuclei in azide ( $NaN_3$ ) are being investigated. Information about the structure of the  $N_3$  group is being sought.

#### 5.20. Magnetic Resonance Studies at the Boulder Laboratories

L. M. Matarrese

Radio & Microwave Materials Section

The purposes of this project are to determine the magnetic energy levels, relaxation times, and transition probabilities of paramagnetic resonance techniques.

An X band EPR spectrometer was completed and improved by addition of automatic frequency control on the sample cavity, a 100 kc field modulation and detection system, and a field scanning device driven by an NMR fluxmeter. A new type of plastic cavity with very thin plated inner walls, for use with the 100 kc system, was designed and constructed. A K-band EPR spectrometer was assembled and operated to provide correlative data. Special cavities for ENDOR (electron-nuclear double resonance) for both X band and K band were designed and are being constructed. The machine calculations of energy levels of manganous ion in calcite were completed; they satisfactorily removed the discrepancies that existed when calculations were made by the more usual approximate methods and proved that the initial spin Hamiltonian used to describe the energy levels was correct. Attempts to find the EPR of ferric ion in zinc fluoride single crystals met with failure. The well-known complex spectrum of an unwanted impurity, manganous ion, was detected in these crystals and may have served to mask the desired spectrum. Interesting EPR spectra were discovered in amethyst, topaz, and aragonite crystals. Attention was concentrated on the amethyst spectrum, and a serious attempt is being made to characterize the spectrum completely and correlate it, if possible, to other known physical phenomena which take place in amethyst. The crystallographic nonuniformity of many specimens of amethyst has created difficulties in this work.

Work on amethyst and topaz spectroscopy is continuing using specimens of quartz doped with ferric and ferrous ions. ENDOR experiments will be carried out on manganous-calcite

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\* This work was supported by the Engineering Research and Development Laboratory, Department of the Army.



system and topaz, which contain nuclear species that interact with the electron spins. Low temperature experiments are planned on these systems and also on the zinc fluoride, in a further search for the iron known to be present. Preliminary investigations on antiferromagnetic copper and cobalt sulfates are planned, which may require use of the cryogenic magnet and millimeter waves.

#### 5.21. Dilatometric Studies of Polymers

J. Powers and F. Quinn,

Macromolecules Synthesis & Structure Section

a.) Polymorphism in Polybutene-1: Studies already completed show that polybutene-1 has at least two melting points and two temperature ranges which differ in their temperature-specific volume relations. The upper range exhibits a crystallization rate-temperature behavior similar to those of polyethylene or polypropylene. The second range is unique and it is suggested that the latter arises from either a crystal-crystal or  $11_3$  helix to a  $3_1$  helix transformation rather than from a further increase in sample crystallinity. The nature of the transition in the latter temperature range is being elucidated by specific volume measurements as a function of temperature and pressure.

b.) Polyptentene-1: Polyptentene-1 shows a maximum in its crystallization rate-temperature curve as determined dilatometrically. The only other example of a maximum obtained dilatometrically is that of natural rubber. Further, preliminary measurements indicate that polyptentene-1 may exhibit polymorphic behavior similar to that of polybutene-1. Measurements of the specific volume of polyptentene-1 as a function of temperature and pressure are planned.

#### 5.22. Field-Emission Studies of the Oxidation of Single-Crystal Metal Whiskers

W. J. Ambs and E. Escalante,

Metal Reactions Section

The purpose of this project is to study the formation of first oxide layers on single crystals.

Iron whiskers were grown by metal sublimation in an ultra-high-vacuum apparatus. A preliminary oxidation experiment showed a distinct cessation of field emission from the  $\{111\}$  plane when oxygen was admitted at low pressures. During the oxidation of nickel, as observed in the field emission microscope, it was found that at temperatures of 500 to 600°C, nickel-oxide whiskers nucleated and grew. These whiskers were substantially larger if the substrate contained dissolved nickel oxide.

#### 5.23. Surface Structure of Vapor-Grown Cadmium Crystals

A. R. Verma (Department of Physics,  
Banaras Hindu University, Varanasi, India)

R. L. Parker, Metal Physics Section

The purpose of this project is to study surface morphology in order to help determine the growth mode of platelets.

Professor Verma's aid in examining the  $\{0001\}$  surfaces of Cd platelets grown at low supersaturations has been enlisted because of his authoritative skill in multiple-beam interferometry of crystal surfaces. This cooperative effort was originated as part of the NBS counterpart-funds program.

Of particular interest is the mechanism by which these platelets grow with no dislocations at all observable by electron transmission microscopy. Whether dislocations, present during growth, slip out of the crystal at some stage before it is examined in the electron microscope should be capable of being determined by optical multiple-beam methods. A number

of small platelets grown here have been sent to Professor Verma and are in the process of being examined.

#### 5.24. Surface Behavior of Silver Single Crystals in Fused Sodium Chloride

J. Kruger, Metal Reactions Section and

K. H. Stern, Electrochemistry Section

The purpose of this project is to investigate fundamental reactions at metal single-crystal surfaces that influence corrosion processes.

In a recent paper J. Kruger and K. H. Stern (1962) have described a study of the effect on a silver single crystal of immersion in fused NaCl at 900°C. In the presence of a temperature gradient both dissolution and dendritic growth of silver occurred. Mass-transfer, resulting from dissolution and deposition, occurred from the hot to the cold end of the crystal and was accounted for by shifts of the equilibria  $2 \text{Ag} + 1/2 \text{O}_2 = 2 \text{Ag}^+ + \text{O}^{2-}$  and  $\text{Ag} + \text{Na}^+ = \text{Ag}^+ + \text{Na}$ . Where the thermal gradient was small, faceted growth of silver crystals epitaxially related to the substrate crystal was observed.

#### 5.25. The Characterization of Silver Iodide Crystals\*

G. Burley, Crystallography Section

Silver iodide has been studied by means of the X-ray diffraction technique in attempts to correlate the structure and various physical properties (Burley, 1962). The wurtzite-zincblende type phase dimorphism at temperatures below 147°C has been investigated and the role of impurities in phase determination has been demonstrated. The photolytic decomposition in the presence of a halogen acceptor, such as n-butyl alcohol, was shown to be related to the formation of a random mosaic structure from a remarkably perfect one. A single crystal structure determination of the hexagonal wurtzite phase revealed no evidence of a statistical displacement of silver atoms from the ideal sites, but rather only a small anisotropic temperature motion of the atoms. All attempts to grow single crystals of the face-centered cubic zincblende phase of silver iodide have been unsuccessful. As has been shown by L. H. Bolz (unpublished) polycrystalline specimens of this phase revealed a primarily negative thermal expansion over the entire temperature range from 4° to 300°K. The results from samples prepared by hydrostatic pressure and by quenching differed considerably, probably due to variation in the number of defects introduced.

### 6. INFORMATION ON CRYSTAL GROWTH AND CHARACTERIZATION

F. Ordway, Crystal Growth Section

A file of data on commercial sources of single crystals and ultra-pure materials was maintained, and information therefrom was supplied to inquirers from NBS and elsewhere. Negotiations were begun for the production, by a chemical data-processing organization, of an index to cover the technical literature for 1962 of interest to the Crystal Growth Section. The objective definition of the range of interest, by which references will be selected, was tested by sample hand searches.

The Oak Ridge National Laboratory of the Atomic Energy Commission has started a Materials Information Center with which close collaboration is being planned.

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\* This work was supported by the National Science Foundation.

## 7. PARTIAL LIST OF PARTICIPANTS

There follows a partial list of scientists engaged in activities described in this note, with indications of their research fields and organizational location within the National Bureau of Standards. The latter may be helpful in making contact with individuals for the purpose of obtaining reprints or further technical information.

### Participants at the Washington Laboratories:

AMBS, William J.: Ph.D. Catholic University, 1961; corrosion by energetic species, oxide mono-layer formation; Metal Reactions Section, Metallurgy Division.

ALLEN, Harry C. Jr.: Ph.D. University of Washington, 1951; crystal structure; Chief, Analytical and Inorganic Chemistry Division.

BARBER, David J.: Ph.D. University of Bristol, Bristol, England, 1959; dislocations and plastic flow in alkali-halide crystals; Crystal Growth Section, Inorganic Solids Division.

BECKER, James: Ph.D. Cornell University, 1957; optical and transport properties of semiconductors; Atomic Physics Section, Solid State Physics Division.

BLUNT, Robert F.: Ph.D. Rice University, 1949; optical properties of solids; Solid State Physics Section, Atomic Physics Division.

BOLZ, Leonard H.: X-ray diffraction on frozen vapors and other solid materials; Crystallography Section, Inorganic Solids Division.

BOWMAN, Horace A.: Cartesian diver; Mass and Scale Section, Metrology Division.

BROWER, William S.: Verneuil process; Crystal Growth Section, Inorganic Solids Division.

BROWN, Walter E.: Ph.D. Harvard University, 1949; solubility and crystallography of calcium phosphate; Dental Research Section, Polymers Division.

BURLEY, Gordon: Ph.D. Georgetown University, 1962; crystallography of silver iodide; Crystallography Section, Inorganic Solids Division.

COHEN, Martin I.: X-ray diffraction studies of crystals grown at high temperatures; Solid State Physics Section, Atomic Physics Division.

COOK, Richard K.: Ph.D. University of Illinois, 1935; acoustics and solid state physics; Sound Section, Mechanics Division.

DESLATTES, Richard D.: Ph.D. Johns Hopkins University, 1959; X-ray spectroscopy; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division.

ESCALANTE, Edward: Field-emission; Metal Reactions Section, Metallurgy Division.

FARABAUGH, Edward N.: Etch pits; Crystal Growth Section, Inorganic Solids Division.

FRANKLIN, Alan D.: Ph.D. Princeton University, 1949; properties of point defects in crystals; Chief, Inorganic Solids Division.

FREDERIKSE, Hans P. R.: Ph.D. Leiden University, Netherlands, 1950; semiconductors at low temperatures; Chief, Solid State Physics Section, Atomic Physics Division.

FRENCH, Judson C.: Electron devices; Electron Devices Section, Instrumentation Division.

FROLEN, Lois: Ph.D. Pennsylvania State College, 1963; Spectroscopy, crystallography, microscopy; Pure Substances Section, Analytical and Inorganic Chemistry Division.



HARDY, Stephen C.: Vapor growth of metal crystals; Metal Physics Section, Metallurgy Division.

HIGIER, Theodore: Resistance of germanium; Electron Devices Section, Instrumentation Division

HOFFMAN, John D.: Ph.D. Princeton, 1949; dielectrics, nucleation rate of polymer crystals; Chief, Dielectrics Section, Electricity Division.

HORTON, Avery T: Crystal growth, impurity retention; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division.

HOWARD, Robert: Ph.D. Oxford, England, 1957; theoretical physics; Metal Physics Section, Metallurgy Division.

KAHN, Arnold H.: Ph.D. University of California, 1955; band structure of rutile crystals, studies of paramagnetic impurities in rutile crystals; Solid State Physics Section, Atomic Physics Division.

KRUGER, Jerome: Ph.D. University of Virginia, 1953; corrosion reactions at metal surfaces; Metal Reactions Section, Metallurgy Division.

MANN, David E.: Ph.D. University of Chicago, 1948; spectroscopy; Chief, Molecular Spectroscopy Section, Physical Chemistry Division.

McMURDIE, Howard F.: Crystallography and chemical phase studies; Chief, Crystallography Section, Inorganic Solids Division.

McNISH, Alvin G.: Precise density determinations for solid materials; Chief, Metrology Division.

NEUMAN, Roslyn C.: Properties of polymers; Dielectrics Section, Electricity Division.

OGBURN, Fielding: Electrochemistry, electrodeposition; Electrolysis and Metal Deposition Section, Metallurgy Division.

ORDWAY, Fred: Ph.D. California Institute of Technology, 1949; studies in X-ray crystallography; Chief, Crystal Growth Section, Inorganic Solids Division.

OREM, Theodore: Mechanisms of corrosion processes; Metal Reactions Section, Metallurgy Division.

PARETZKIN, Boris: Study of perfection of single crystals by means of X-ray diffraction; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division.

PARKER, Robert L.: Ph.D. University of Maryland, 1960; growth of crystals; Metal Physics Section, Metallurgy Division.

PASSAGLIA, Elio: Ph.D. University of Pennsylvania, 1955; Mechanical relaxation processes in polymers; Polymer Physics Division.

PEISER, H. Steffen: Crystallography and crystal chemistry; Chief, Crystal Chemistry Section, Analytical and Inorganic Chemistry Division.

POLLACK, Gerald L.: Ph.D. California Institute of Technology; low temperature physics; Crystal Growth Section, Inorganic Solids Division.

POWERS, Joseph: Ph.D. University of Massachusetts, 1961; kinetics, morphology, and mechanism of crystallization of polymers; Macromolecules Synthesis and Structure Section, Polymers Division.

QUINN, Fred A.: Crystallization rate of high polymers; Macromolecules Synthesis and Structure Section, Polymers Division.

ROBBINS, Carl R.: Phase-rule equilibria of inorganic systems; Crystallography Section, Inorganic Solids Division.

ROBERTS, D. Ellis: High-temperature crystal growth; Solid State Physics Section, Atomic Physics Division.

ROSS, Galen S.: Nucleation, crystal growth; Pure Substances Section, Analytical and Inorganic Chemistry Division.

ROTH, Robert S.: Ph.D. University of Illinois, 1951; X-ray diffraction studies in connection with phase equilibria; Crystallography Section, Inorganic Solids Division.

RUFF, Arthur W.: Dislocations and etch pits; Metal Physics Section, Metallurgy Division.

SAYLOR, Charles P.: Ph.D. Cornell University, 1928; precise physical characteristics of compounds, accurate microscopic measurements of optical properties; Analytical and Inorganic Chemistry Division.

SCHOOLEY, James F.: Ph.D. University of California, 1961; crystal growth for low-temperature paramagnetic studies; Cryogenics Section, Heat Division.

SCHOONOVER, Irl C.: Ph.D. Princeton University, 1933; research administration; NBS Director's Office.

SCRIBNER, Bourdon F.: Analytical applications of optical and X-ray spectroscopy; Chief, Spectrochemistry Section, Analytical and Inorganic Chemistry Division.

STRASSBURGER, John: Crystal growth from solution; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division.

SWANSON, Howard E.: Physical chemistry, X-ray diffraction; Crystallography Section, Inorganic Solids Division.

SWARTZENDRUBER, Lydon J.: Solid state physics; Electron Devices Section, Instrumentation Division.

TIGHE, Nancy: Defects by means of electron microscopy of non-metallic crystals; Physical Properties Section, Inorganic Solids Division.

TORGESEN, John L: Ph.D. Columbia University, 1942; crystal growth, impurity retentions, crystal properties; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division.

VAN VALKENBURG, Alvin: High pressure transitions; Crystallography Section, Inorganic Solids Division

WACHTMAN, Jack, Jr., Ph.D. University of Maryland, 1961; mechanical and electrical properties of crystals; Physical Properties Section, Inorganic Solids Division

#### Participants in the Boulder Laboratories:

DALKE, J L: The characterization of materials at radio frequencies; Chief, Radio and Microwave Materials Section, Radio Standards Physics Division.

GRUZENSKY, Paul M.: Ph.D. Oregon State College, 1959; physical chemistry and high purity materials; Radio and Microwave Materials Section, Radio Standards Physics Division.

JEFFERSON, Clinton F.: Ph.D. University of Michigan, 1959; solid state solutions for ferrimagnetic characteristics; Radio and Microwave Materials Section, Radio Standards Physics Division.

MATARRESE, Lawrence M.: Ph.D. University of Chicago, 1954; solid state physics; EPR and other resonance spectroscopy related to solid state mechanisms; Radio and Microwave

Materials Section, Radio Standards Physics Division.

WELLS, Joseph S.: Microwave physics; solid state physics as it relates to ENDOR and NMR; Radio and Microwave Materials Section, Radio Standards Physics Division.

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U. S. DEPARTMENT OF COMMERCE

Luther H. Hodges, *Secretary*

NATIONAL BUREAU OF STANDARDS

A. V. Astin, *Director*



## THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

### WASHINGTON, D. C.

**Electricity.** Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics. High Voltage.

**Metrology.** Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

**Heat.** Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics. Radiation Physics. X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

**Analytical and Inorganic Chemistry.** Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research. Crystal Chemistry.

**Mechanics.** Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

**Polymers.** Macromolecules: Synthesis and Structure. Polymer Chemistry. Polymer Physics. Polymer Characterization. Polymer Evaluation and Testing. Applied Polymer Standards and Research. Dental Research.

**Metallurgy.** Engineering Metallurgy. Microscopy and Diffraction. Metal Reactions. Metal Physics. Electrolysis and Metal Deposition.

**Inorganic Solids.** Engineering Ceramics. Glass. Solid State Chemistry. Crystal Growth. Physical Properties. Crystallography.

**Building Research.** Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials. Metallic Building Materials.

**Applied Mathematics.** Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

**Data Processing Systems.** Components and Techniques. Computer Technology. Measurements Automation. Engineering Applications. Systems Analysis.

**Atomic Physics.** Spectroscopy. Infrared Spectroscopy. Far Ultraviolet Physics. Solid State Physics. Electron Physics. Atomic Physics. Plasma Spectroscopy.

**Instrumentation.** Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

**Physical Chemistry.** Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Elementary Processes. Mass Spectrometry. Photochemistry and Radiation Chemistry.

Office of Weights and Measures.

### BOULDER, COLO.

**Cryogenic Engineering Laboratory.** Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

### CENTRAL RADIO PROPAGATION LABORATORY

**Ionosphere Research and Propagation.** Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services. Vertical Soundings Research.

**Radio Propagation Engineering.** Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

**Radio Systems.** Applied Electromagnetic Theory. High Frequency and Very High Frequency Research. Frequency Utilization. Modulation Research. Antenna Research. Radiodetermination.

**Upper Atmosphere and Space Physics.** Upper Atmosphere and Plasma Physics. High Latitude Ionosphere Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

### RADIO STANDARDS LABORATORY

**Radio Physics.** Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time-Interval Standards. Radio Plasma. Millimeter-Wave Research.

**Circuit Standards.** High Frequency Electrical Standards. High Frequency Calibration Services. High Frequency Impedance Standards. Microwave Calibration Services. Microwave Circuit Standards. Low Frequency Calibration Services.

