A UNITED STATES
DEPARTMENT OF
COMMERCE
PUBLICATION

NBS TECHNICAL NOTE 798

Collaborative Research Program Between NBS and Indian Scientific Institutions

Special Foreign Currency Program 1973 Status

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Part of the Center for Radiation Research.

[3] Located at Boulder, Colorado 80302.

[4] Part of the Center for Building Technology.

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Edited by

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Doris M. Bluebond

Special Foreign Currency Program
Office of International Relations
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Washington, D.C. 20234

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Issued November 1973

National Bureau of Standards Technical Note 798

Nat. Bur. Stand. (U.S.), Tech. Note 798, 139 pages (Nov. 1973)

CODEN: NBTNAE

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
(Order by SD Catalog No. C13.46:798). Price $1.50

FOREWORD

For several years the National Bureau of Standards has collaborated with technical institutions in India through research projects conducted largely in Indian institutions, and by occasional exchange visits of Indian and NBS scientists and engineers. This program has been made possible through funds available under the Special Foreign Currency Program (PL-480), in which the United States has sold agricultural commodities and other products to India, accepting payment in rupees which remain on deposit in that country for use in ways that are mutually agreed upon. One of these uses is to support research of interest to both nations.

The NBS sponsored research program in India is reviewed in this publication. For each project included in this program, the report summarizes the project goals and some of the major results; a list of publications that resulted from the collaborative effort is included. The names of the principal investigators in India and of the National Bureau of Standards monitors are also included. The review should provide basic information from which scientists and scientific administrators may form opinions on the value and efficacy of such programs. Officials concerned with international science and technology will wish to examine this case history of international scientific cooperation.

Our objective within NBS is to evaluate the ways in which this program has contributed to the accomplishment of the NBS mission and to the advancement of science and technology. Each participating Indian institution can use the report to help evaluate the ways the program has contributed to the achievement of its own goals.

We at NBS have concluded that this program has helped us to achieve some of our institutional goals, has contributed to the advance of science and technology, and has established lasting technical friendships between many NBS scientists and colleagues in India. We trust that our Indian associates share our view.

Richard W Roberts

Richard W. Roberts
Director, National Bureau of Standards

ABSTRACT

An overview is given of grants awarded by the National Bureau of Standards under the Special Foreign Currency Program in India, authorized by Public Law 480 and its amendments. Each grant is identified by title, principal investigator, institution in India, NBS monitor charged with working in close technical touch with the project in India, and the monitor's organizational unit within NBS. The relevant work is then described briefly under the three headings "Summary Description of Project Goals," "Results and Implications to Date," and "List of Publications that Resulted from the Project." To demonstrate the wide use of such grants over the entire Program Structure of NBS, the grant descriptions are ordered by the elements of that Program Structure. Editorial comment on the significance and purpose of the NBS/SFCP grant program is confined to a Foreword and Introduction. The editors judge this grant program to have had a high benefit to cost ratio from the viewpoint of NBS.

Key words: Binational research cooperation; international scientific cooperation; India science and technology; physical science research administration; research planning; scientific research abstracts; Special Foreign Currency Program.

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1. INTRODUCTION

Information on scientific research and technical innovation is normally published in specialized journals and a literature devoted to abstracts of such reports enables a specialist to find material related to his own interests. The present publication, a collection of summaries of scientific research, has a purpose different from those associated with such conventional publications. We, the editors, have assembled evidence on which a cooperative scientific program can be evaluated; we are not trying to inform scientists in specialized fields about recent scientific news. We are viewing the overall Special Foreign Currency Program of the National Bureau of Standards in India over roughly the past five years. We are here presenting not our own assessment of the program but are, rather, attempting to present sufficient information in a useful form for the program to be evaluated by interested persons. In this connection, requests for more detailed additional information would always be welcome as would comments and criticisms of the program. We are ourselves aware that certain features of the program could be improved in the future.

Special assessment of this program is needed because it is an unusual one. Such an assessment could well be done from a number of viewpoints; for instance, those of the grantor and grantee institutions as well as from those relating to the broad national goals of each country. The program has already been carefully examined from the point of view of the NBS by NBS management and found to be of assistance in carrying out its mission. The program supplements the research output of the NBS and enhances international collaboration involving its scientists. The program may have other significance: it demonstrates a technique by which a smaller less wealthy country can keep in touch with a larger country when both are highly developed scientifically; and, in some instances, it may offer the opportunity to develop a specialized competence in one of the two countries where previously such competence did not exist.

Staff members of NBS have reacted favorably to this program. A number of NBS personnel have commented that their own individual SFCP projects have been successful and relevant, and they have very strongly encouraged us to present them with sufficient information to allow them to take a broader view of the program so as to enable them to see it in its entirety. This Technical Note is an attempt at presenting the requisite information, relating to grants at Indian institutions, for producing such an overview. This Technical Note follows similar publications relating to such NBS grants in Israel and Yugoslavia.

A person attempting an analysis and evaluation of this Program need not necessarily concern himself with administrative details. For those who are interested, the editors have included some background administrative and historical material in Appendix I. To carry out its responsibilities under the various Acts of Congress, by which U.S. federal agencies have had the opportunity to use certain excess foreign currencies in India for the pursuit of scientific research and technical development work, the National Bureau of Standards has adopted guidelines for its Program, as also reprinted in Appendix I.

The reader examining the program from the grantor country's point of view has the opportunity to judge whether it has increased the research output of NBS appreciably and, if so, whether this has been in useful directions; and also, whether U.S. national goals were served. To make this task easier we have assembled the sections of this Technical Note into categories identified by the NBS Program Structure under which all NBS projects are classified. The list of these Program Structures appears in Appendix II.

The reader oriented to the Indian viewpoint, on the other hand, should ask whether new techniques really have been brought to India by these projects and whether techniques already in existence have been given the opportunity to develop. Questions should be raised, such as: Have new competences been built up and old ones strengthened or have scientific and technological talents been diverted from the real national goals of India towards the longer-range goals of the USA? Have neighboring fields been enriched in India by cross-fertilization, have applications in industry been sparked, and has the program helped to provide India with a broadly based infrastructure of science and technology? Have graduate students assigned to the projects received training which ultimately will benefit India?

Readers with more specific viewpoints will ask such questions as:

1. Were the projects in the fields familiar to you well executed?
2. Did the senior investigators demonstrate exceptional competence which could be of special service in the future?

3. Did the projects contribute to problems of known importance to science, technology, or society?
4. Is there evidence that contact between U.S. and Indian scientists was intellectually stimulating and helpful perhaps in related work?
5. Does the program appear to have contributed to forming a good climate for scientific progress and technological innovation?
6. Did the program help to widen the horizons of scientists towards application of their expertise to urgent national needs?
7. Does this report suggest that bi-national programs of this type should be developed for mutual benefit?

This list of questions is certainly not exhaustive nor are their answers by any means obvious.

This Technical Note is addressed most particularly to scientifically trained science administrators. In it the editors have summarized approximately $950,000 worth of funded research. In many instances the projects were considered valuable enough by Indian officials for them to have often augmented NBS support from other sources. Salary costs of faculty members were provided by the Indian institutions.

The NBS monitor has been strongly encouraged to carry on direct communication with the principal investigator. Visits by NBS monitors to India have broadened the basis of interaction. Whenever it has become necessary, for scientific reasons, for an NBS monitor to visit his project in India, he has been strongly urged to visit as many additional scientific institutions and laboratories as possible and to describe, in writing, on his return, his view of the scientific competences and the particular strengths and weaknesses which he observed. In addition to serving to broaden the outlook of the NBS monitor, the visits increase the contacts between Indian scientists and the NBS staff, thereby enabling the Indian scientists to understand NBS better. This increases the likelihood that Indian scientists involved in the program will, to a certain extent, insert into their projects an NBS point of view in addition to their own. By careful planning of such NBS staff visits their cost has been restrained to less than 2 percent of project funds available, despite the costly airfare.

Visits by Indian principal investigators to NBS are rare events because the Government of India requires special justification to give such travel the high priority needed to use scarce foreign currency reserves. NBS collaborators would have preferred to see more Indian colleagues in their laboratories at NBS, but they realize that the Indian authorities necessarily view this program in a context of many competing urgent needs for foreign currency.

Whereas the effective output from several projects might have been enhanced by such visits, the actual accomplishments are nevertheless significant as is clearly shown in the succeeding pages of this Technical Note. For example; new spectroscopic data have been recorded, collections of critically evaluated data on physical properties have been made available, standard reference materials have been developed, nuclear cross-sections and angular correlations have been studied, analytical procedures for estimating trace elements in glasses have been elucidated, catalytic activities have been related to the structures of oxides, high temperature transformations in oxides have been examined, new metallo-organic compounds have been prepared, methods for the suppression of electrical breakdown at high voltages have been scrutinized, and types of building structures have been observed under dynamic and static loads.

Project Title: ULTRASONIC DISPERSION AND ABSORPTION

Principal Investigator: Dr. S. K. Kor

Institution: Allahabad University, Allahabad

NBS Monitor: Dr. M. D. Scheer

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

Ultrasonic dispersion and absorption will be studied in pure liquids, electrolytic solutions, and liquid crystals in order to determine the relaxation kinetics for processes which are characteristic of these systems. For example, molecular and ion-association rates can be determined in polar liquids and electrolytic solutions by this method. The study of liquid crystals by this technique is a new area of investigation and may lead to important new insights into the behavior of these interesting substances. The color changes in liquid crystals are very temperature sensitive and can be used for the detection of microwave heating, of chemical vapors, and of ultraviolet and infrared radiation.

Results and Implications to Date

Ultrasonic absorption and velocity measurements have been made in the following alkali halides: NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbI, CsI, LiF, and LiCl in mixed solvents using a pulse technique at 25°C. The total absorption in the solvent can be written as:

$$(\alpha/f^2)_{\text{total}} = (\alpha/f^2)_{\text{shear viscosity}} + (\alpha/f^2)_{\text{structural}}$$

as the contributions due to thermal conduction and thermal relaxation are negligible. Since the alkali halides show practically no association, absorption in solution is assumed to be controlled by the above two factors. The contribution due to shear viscosity is obtained from the relation:

$$(\alpha/f^2)_{\text{shear viscosity}} = \frac{8\pi^2}{3} \frac{\eta_s}{\rho c^3}$$

Using the above two relations, a structural contribution can be obtained. For the same halide ion, the shear viscosity is found to decrease in the order Li, Na, K, Rb whereas for the same cation the decrease is in the order Cl, Br, I.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

Ultrasonic absorption and velocity measurements have been made in eugenol in the temperature range 0 - 50°C at 45 MHz. The various contributions to the total ultrasonic absorption are:

$$\begin{aligned}(\alpha/f^2)_{\text{total}} &= (\alpha/f^2)_{\text{shear}} + (\alpha/f^2)_{\text{comp.}} + (\alpha/f^2)_{\text{thermal}} \\ &= \frac{2\pi^2}{\rho c^3}\left(\frac{4}{3}\eta_s + \eta_c\right) + (\alpha/f^2)_{\text{thermal}}\end{aligned}$$

where η_s and η_c are the shear and compressional viscosities respectively. Work is in progress on the various contributions of ultrasonic absorption in eugenol.

Future plans consist of work in the following directions:

(i) Ultrasonic absorption and velocity measurements in pure liquids and interpretation of the results.

(ii) Ultrasonic absorption and velocity measurements in liquid crystals. Arrangements for making measurements in the high temperature region are in progress.

(iii) Ultrasonic absorption and velocity measurements in electrolytic solutions and the study of ion-association. Ion-association is presently not clearly understood. Yet it is a phenomenon which influences many chemical processes.

List of Publications that Resulted from the Project

This project was funded only recently so that there are no publications as yet.

A.1.* PHYSICAL MEASUREMENT METHODS, UNITS, AND STANDARDS

Project Title: DEVELOPMENT OF HIGH PRESSURE TECHNIQUES AND SOME APPLICATIONS

Principal Investigators: Professor R. S. Krishnan
Professor E. S. Rajagopal

Institution: Indian Institute of Science, Bangalore

NBS Monitor: Dr. P. L. M. Heydemann

NBS Institute or Center and Division: Institute for Basic Standards
Heat Division

Summary Description of Project Goals

The main objective of the project is to develop instrumentation for the generation of high pressures, in stages, up to 100 kbar, and to use the equipment to measure physical properties such as optical and dielectric properties, critical phenomena and phase transitions. Studies of resistivity and nuclear quadrupole resonance (NQR) will also be attempted. All these measurements are now carried out in the laboratory at 1 atm. conditions.

Results and Implications to Date

Work on the project started in October, 1972. An arrangement is being set up to study the optical behavior of materials up to about 7 kbar. The substance to be studied is contained between a pair of Bridgman opposed anvils, and is pressurized by a standard hydraulic press. The optical path is parallel to the pressure axis, thereby reducing the effect in the studies of pressure gradients across the anvil face. Sapphire anvils, to be used in the final measurements, are being ground. Tungsten carbide anvils for use up to 40 kbar are being procured. Preliminary trials upto 1 kbar have been performed using simple glass anvils. A tubular furnace surrounding the anvil assembly is used to vary the temperatures.

The preliminary design and the drawings for a piston-cylinder apparatus are being made.

Calculations on the stability of the diamond structure at high pressures has been completed. The bond bending and bond stretching force constants at high pressures have been estimated for diamond, Si, Ge, CaAs and GaSb. It is found that their ratio has a critical value ∿ 0.04 to 0.08 when the structural change occurs.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

The NBS monitor states that the work performed in the High Pressure Group of the NBS Pressure and Vacuum Section and at the Indian Institute of Science is directed toward the establishment of a high pressure scale. In the past considerable effort was spent on the investigation of phase transitions and other properties of materials that could be used as fixed points on the pressure scale. Now most of this activity will be moved to IIS and concentration will be instead on the development of a transfer gage for high pressures. This transfer gage will then be used both at NBS and at IIS to tie the fixed points to the scale.

NBS is particularly interested in the IISc work on NQR. Several years ago NBS began to study the possibility of using NQR as an extremely stable transfer device. Lack of manpower forced abandonment of the project at NBS, but it is now being revived under this grant.

List of Publications that Resulted from the Project

1. S. N. Vaidya, "Stability of Diamond and Zinc Blende Structures at High Presssures," Current Science (accepted for publication).

A.5.* STANDARD REFERENCE DATA

Project Title: PROPERTIES OF ELECTROLYTES IN NONAQUEOUS MEDIA

Principal Investigators: Dr. Mihir Nath Das
Dr. Kiron Kumar Kundu

Institution: Jadavpur University, Calcutta

NBS Monitors: Dr. Roger G. Bates (up to September 1969)
Dr. John K. Taylor (1969-70)
Dr. Richard A. Durst (1970)

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

The main object of the project was to collect standard physico-chemical data for solutions of electrolytes in nonaqueous solvents and their aqueous mixtures, and as an essential prerequisite to such studies, to develop suitable methods for accurate measurements of the desired quantities. The investigations under the project have yielded useful physico-chemical data which should be of value for an understanding of the properties of electrolyte solutions in general, and are also likely to prove useful in relation to some electrochemical processes of technological importance.

Results and Implications to Date

The experimental work mainly involves the determination of the standard potentials of the silver-silver halide (chloride, bromide, and iodide) electrodes and M/M^+ electrodes (M = Li, Na, K, and Cs) in ethylene glycol (EG) and its aqueous mixtures as well as in propylene glycol (PG) and its methanolic mixtures. The thermodynamic dissociation constants of several acids of different charge types have also been determined by potentiometric or spectrophotometric measurements. The related thermodynamic quantities have been evaluated from the data obtained.

A. Standard electrode potentials in ethylene glycol (EG) - water solvent system and related thermodynamic quantities.

(i) The standard potentials (E^o) of the Ag-AgCl electrode in EG and its aqueous mixtures of varying compositions have been determined at different temperatures (5-45°C) using a cell of the type A [1][1].

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

[1] Figures in square brackets indicate the publication reference at the end of this project review.

$Pt/H_2(g, 1\ atm)/HCl(m), solvent/AgCl\text{-}Ag$ ... type (A)

For the Ag-AgI electrode [4, 13] and the Ag-AgBr electrode (in pure EG) [2] the cell of the type A was found unsuitable, and a cell of the type B was used.

$Pt/H_2(g, 1\ atm)/HOAc(m_1), NaOAc(m_2), NaX(m_3), solvent/AgX\text{-}Ag$ ... type (B), where X = Br or I and HOAc denotes acetic acid, whose dissociation constants in the different solvent media were first determined using the Ag-AgCl electrode in the cell of the type B, E^o of the Ag-AgCl electrode being known from previous independent measurements with cells of the type A. The E^o_m values (molal scale) so obtained at different temperatures have been fitted in the form of Harned-Robinson type equations, using the least squares method:

$$E^o_m = A - B(t - 25) - C(t - 25)^2 \quad \ldots \quad (1),$$

where t denotes the temperature on the Celsius scale.

The standard potentials on the mole fraction scale (E^o_N) were calculated from E^o_m, and the standard free energy of transfer (ΔG^o_t) at 25°C of one mole of HX from water to another medium was evaluated from E^o_N, by using the reported value of E^o_N for water. From the temperature coefficients of the standard potentials, the standard entropy of transfer (ΔS^o_t) and hence the standard enthalpy of transfer (ΔH^o_t) at 25°C were also computed, using equation (1) [13]. For HBr, the relevant E^o date previously determined in this laboratory have been used.

(ii) The standard potentials of M/M^+ electrodes (M = Li, Na, K, and Cs) [6,12] in Eg and its aqueous mixtures of varying composition have been determined at 25°C, using a cell of the type C in conjunction with a cell of type D, the concentration of the alkali metal in the amalgam being the same in C and D.

$M_y(Hg)/MBr(m), solvent/AgBr\text{-}Ag$ ... type (C)

$M_y(Hg)/MBr(m), water/AgBr\text{-}Ag$ ... type (D)

The activities of the amalgams used were evaluated from the emf's of the cell D by using the reported activity of MBr at the respective values of m (m = 0.10, 0.20, and 0.50) in aqueous solutions, and the standard potentials of M/M^+ and Ag-AgBr electrodes in water. These values were used to compute the standard emf's $({}_sE^o_{cell})_E$ of the cell E.

M/MX, solvent/AgX-Ag ... type (E),

where X = Br.

By coupling the standard potentials of M/M^+ electrodes with those of the Ag-AgCl and Ag-AgI electrodes determined earlier, the values of $({}_sE^o_{cell})_E$ were obtained for X = Cl and I, for the different media. The values of $({}_sE^o_{cell})_E$ on the mole fraction scale were utilized to evaluate the standard free energies of transfer, $\Delta G^o_t(MX)$, of MX electrolytes from water to glycol and its aqueous mixture [12].

B. Thermodynamic dissociation constants of some acids of different charge types in ethylene glycol (EG) - water solvent system.

A cell of the type F has been used to determine the acidic dissociation constants of ammonium and several alkylammonium ions in pure EG at nine temperatures (5-45°C) [3].

$Pt/H_2(g,\ 1\ atm)/BH^+Br^-(m_1),\ B(m_2)$, solvent/AgBr-Ag ... type (F)

where B is an amine base.

The pK_{BH^+} values at different temperatures have been fitted into Harned-Robinson type equations by the method of least squares.

$$pK_{BH^+} = a/T + b + cT \quad \ldots \quad (2)$$

The standard thermodynamic quantities, ΔG^o, ΔH^o, ΔS^o, and $\Delta C_p{}^o$ for the dissociation of the acids in EG have been computed from the constants of equation (2).

The dissociation constants of protonated tris(hydroxymethyl)aminomethane (tris. H^+), and monoethanolamine have been determined at different temperatures using a cell of type F, in a series of aqueous mixtures of EG. The constants a, b, and c of equation (2) have been calculated.

The dissociation constants (K_a) of protonated m- and p- mitroanilines (BH^+) and thymolsulphonphthalein (H_2A and HA^-) have been determined at 25°C in aqueous mixtures of EG by spectrophotometric measurements [14].

C. Standard electrode potentials in "isodielectric" media comprising propylene glycol (PG) and methanol.

(i) The standard potentials of the Ag-AgCl electrode in PG [2] and its methanolic mixtures [8,15] (which serve as nearly isodielectric media) have been determined at different temperatures using a cell of the type A. The E_m^o values of the Ag-AgCl electrode at different temperatures have been fitted in equation (1). The standard free energies (ΔG_t^o), enthalpies (ΔH_t^o), and entropies (ΔS_t^o) of transfer of one mole of HCl from methanol to PG and its methanolic mixtures have been calculated.

The standard potentials of the Ag-AgBr electrode in PG-methanol mixtures [8] have been determined at 25°C, using a cell of the type B, the required K_a values of acetic acid in the different media having been obtained as in Section A (ii).

(ii) The standard potentials of M/M^+ (M = Li, Na, K) electrodes in PG-methanol solvent system [10] have been determined at 25°C by using cells of the types C and D. These values have been utilized, as in Section A(ii), for computing the standard emf's $({}_sE^o{}_{cell})_E$ of the cell E (for X = Cl and Br) and hence the standard free energy changes $\Delta G_t^o(MX)$ accompanying the transfer of MX from methanol to the other media.

D. Thermodynamic dissociation constants of some acids in "iso-dielectric" media comprising methanol and propylene glycol (PG).

The dissociation constants of benzoic acid, protonated tris(hydroxymethyl)-aminomethane and p-nitroanilinium ion (p.n.a.H^+) have been determined at 25°C in methanol-PG solvent system by emf measurements of suitable galvanic cells in the first two cases, and by spectrophotometric measurements for p.n.a.H^+ [11].

E. Miscellaneous measurements relating to proton transfer equilibria in glycolic media.

(i) Autoprotolysis constants:

The autoprotolysis constants (K_s) of ethylene glycol (EG) and propylene glycol (PG) have been evaluated at different temperatures. The pK_s values can be expressed in the form of equation (2) as a function of temperature on the Kelvin scale [5].

The autoprotolysis constants of methanolic mixtures of PG [9] have been determined at 25°C.

(ii) Acidity Functions (H_-) in ethylene glycol (EG):

Acidity function (H_-) scales have been set up for glycoxide solutions of lithium (0.10 - 1.0 M) and sodium (0.10 - 3.0 M) in EG at 25°C by the use of several nitrosubstituted aniline and diphenylamine indicators [7]. The pK values of the indicator acids used referred to EG are as follows: (1) 2,4,4'-trinitrodiphenylamine = (14.35); (2) 2,4,3'-trinitrodiphenylamine = (14.95); (3) 6-bromo-2,4'-dinitroaniline = (16.185); (4) 2,4-dinitrodiphenylamine = (16.445).

F. Solvent effects on the electrolytes and protonation equilibria in glycolic media.

Attempts have been made to analyze the thermodynamic quantities obtained from the above studies in the light of solute-solvent and solvent-solvent interactions.

The values of $\Delta G_t^o(HX)$ at 25°C for the transfer from water to EG and its aqueous mixtures have been split up into the components for the individual ions, $\Delta G_t^o(i)$, by a method of extrapolation essentially based on the Born equation. By using the values of $\Delta G_t^o(\bar{X})$ so obtained, the values of $\Delta G_t^o(i)$ for the alkali metal ions (M^+) at 25°C have been evaluated. For a better understanding of the solute-solvent interactions involved, the "chemical" contributions, $\Delta G_{t,ch}^o(i)$, for M^+ and X^- ions were evaluated by subtracting from $\Delta G_t^o(i)$ the electrostatic contributions obtained on the basis of the Born equation by using the respective crystallographic radii of the ions. The results indicate that cations are glycophilic and the anions hydrophilic [13].

The values of $\Delta S_t^o(i)$ as well as $\Delta S_{t,ch}^o(i)$, and hence of $\Delta H_t^o(i)$ and $\Delta H_{t,ch}^o(i)$, were also obtained in a similar manner. The results tend to suggest that unlike monohydric alcohols, glycol in the initial stages of addition to water does not promote enhanced structure in water, but on further addition, glycol causes breakdown of water structure like other alcohols [13].

The ΔG_t^o values of the MX electrolytes for the transfer from methanol to PG and its methanolic mixtures have likewise been split up into $\Delta G_t^o(i)$ for M^+ and X^-, and hence $\Delta G_t^o(H^+)$ has also been evaluated. The media comprising methanol and PG being very nearly isodielectric, the electrostatic contributions to $\Delta G_t^o(i)$ are expected to be negligibly small, and hence the $\Delta G_t^o(i)$ values directly reflect the "chemical" effects of the solvents on the transfer process. The results indicate that the cations are methanophilic whereas the anions are glycophilic [10].

The values of $\Delta S_t^o(HCl)$ and $\Delta H_t^o(HCl)$ suggest that when PG is added to methanol, or vice versa, in either extreme region there occurs a breakdown of the individual solvent structures, releasing monomeric forms of the solvent dipoles. In the intermediate region, however, the data suggest the formation of some sort of hydrogen-bonded clusters among the solvent dipoles [15].

The thermodynamic quantities accompanying the dissociation of the different substituted ammonium ions in ethylene glycol indicate that, besides the inductive effect, the solvophilicity of the substituents towards glycol plays a dominant role in the overall process [3].

The thermodynamic quantities accompanying the self-ionization of EG and PG and the chemical contributions to these quantities as evaluated on the basis of the Born equation indicate the absence of any water-like characteristic structure in these solvents in spite of possible larger association due to hydrogen bonding [5]. The autoprotolysis constants of PG-methanol mixtures at 25°C suggest that the acidity of the mixed solvent increases and the basicity decreases as the proportion of PG is increased [9].

The understanding of the solvent effect on the proton transfer equilibria involving a conjugate acid-base pair A and B becomes relatively easier when one considers the free energy change, $\Delta G_t^o\left[A - B\right]_{sys}$, accompanying the transfer process (3) from a reference solvent S_o to any other solvent S.

$$S_oH^+(s_o) + S(s) + A(s) + B(s_o) = S_o(s_o) + SH^+(s) + A(s_o) + B(s) \quad \ldots (3)$$

where (s) and (s_o) indicate the substances in their standard states in the solvent S and the reference solvent S_o respectively. Thus

$$\Delta G_t^o \left[A - B\right]_{sys} = 2.303\ RT \left[p\,({}_sK_a)^N_A - p({}_{s_o}K_a)^N_A \right]$$

$$= \Delta G_t^o(H^+) + \Delta G_t^o(B) - \Delta G_t^o(A) \qquad \ldots \quad (4),$$

where $\Delta G_t^o(H^+)$ stands for the free energy change accompanying the process (5), i.e. the transfer of H^+ from the standard state in the reference solvent S_o to the standard state in the solvent S.

$$S_oH^+(s_o) + S(s) \longrightarrow SH^+(s) + S_o(s_o) \qquad \ldots \quad (5)$$

The solvent effects on the dissociation of protonated tris and meta- and para- nitroanilines ($A = BH^+$) in EG-water mixtures [14] at 25°C have been interpreted in terms of the standard free energies of transfer (ΔG_t^o), from water to the aqueous glycol solvents, of the uncharged bases (B), evaluated from the measured solubilities, of the hydrochlorides of the bases (B, HCl), computed from the corresponding values for HCl and also the individual ions assessed from the previous values of $\Delta G_t^o(Cl^-)$.

Similarly the solvent effects on the dissociation of protonated tris and para-nitroaniline ($A = BH^+$) and of benzoic acid ($A = HA$ and $B = A^-$) in PG-methanol solvent system at 25°C have also been interpreted [11].

The overall behavior of the different protonated amines with different chemical nature and also with different solvophilism is found to be largely dictated by the specific solute-solvent interactions, besides the effect of the relative solvent "basicities" as reflected in the values of $\Delta G_t^o(H^+)$ for the different media. It also appears that the protonic character of the hydroxylic hydrogen atom is weaker in ethylene glycol than in water, whereas the negative charge density on the oxygen atom is larger in glycol. Thus water is more "acidic" and less "basic" than ethylene glycol. Methanol, on the other hand, appears to be less "acidic" and more "basic" than propylene glycol.

List of Publications that Resulted from the Project

1. Utpal Sen, K. K. Kundu, and M. N. Das, "Standard Potentials of Ag-AgCl Electrode in Ethylene Glycol and its Aqueous Mixtures at Different Temperatures and Related Thermodynamic Quantities," J. Phys. Chem., 71 3665 (1967).
2. K. K. Kundu, P. K. Chattopadhyay, Debabrata Jana, and M. N. Das, "Standard Potentials of Ag-AgX (X = Cl or Br) Electrodes in Glycol Solvents at Different Temperatures and Related Thermodynamic Quantities," J. Chem. Eng. Data, 15, 209 (1970).
3. K. K. Kundu, P. K. Chattopadhyay, and M. N. Das, "Thermodynamics of Proton Transfer Processes Involving Ammonium and Substituted Ammonium Ions in Ethylene Glycol," J. Chem. Soc. (A), 2034 (1970).
4. K. K. Kundu, Debabrata Jana, and M. N. Das, "Standard Potentials of Ag-AgBr Electrode in Propylene Glycol and of Ag-AgI Electrode in Ethylene and Propylene Glycols at Different Temperatures and Related Thermodynamic Quantities," J. Phys. Chem., 74, 2625 (1970).
5. K. K. Kundu, P. K. Chattopadhyay, Debabrata Jana, and M. N. Das, "Thermodynamics of Self-Ionization of Ethylene and Propylene Glycols," J. Phys. Chem., 74, 2633 (1970).
6. K. K. Kundu and A. K. Rakshit, "Standard Potentials of Cs/Cs^+ Electrode in Ethylene Glycol and 50% Glycol-Water Mixtures and Test of Strehlow's Method for Standard Free Energy of Transfer for Individual Ions from Water to these Solvents," Indian J. Chem., 9, 439 (1971).
7. K. K. Kundu and Lakshmi Aiyar, "Acidity Functions (H_-) of Lithium, Sodium and Potassium Glycoxide Solutions in Ethylene Glycol," J. Chem. Soc. (A), 40 (1971).
8. K. K. Kundu, A. L. De, and M. N. Das, "Studies in Iso-dielectric Media, Part I, Standard Potentials of Ag-AgX (X = Cl or Br) Electrodes in Methanol-Propylene Glycol Media," J. Chem. Soc (Dalton), 373 (1972).
9. K. K. Kundu, A. L. De, and M. N. Das, Ibid. Part II, "Autoprotolysis Constants of Methanol-Propylene Glycol Mixtures at 25°C," J. Chem. Soc. (Dalton), 378 (1972).
10. K. K. Kundu, A. K. Rakshit, and M. N. Das, Ibid. Part III, "Standard Potentials of M/M^+ ($M = Li, Na, K$) Electrodes in Methanol-Propylene Glycol Solvent System," J. Chem. Soc. (Dalton), 381 (1972).

11. K. K. Kundu, A. L. De, and M. N. Das, Ibid. Part IV, "Solvent Effect on Proton Transfer Equilibria of Some Acids in Methanol-Propylene Glycol Solvent System at 25°C," J. Chem. Soc. (Dalton), 386 (1972).

12. K. K. Kundu, A. K. Rakshit, and M. N. Das, "Standard Potentials of Li/Li^{+}, Na/Na^{+} and K/K^{+} Electrodes in Ethylene Glycol and its Aqueous Mixtures at 25°C and Related Thermodynamic Behaviour of the Alkali Halides," Electrochim. Acta, 17, 1921 (1972).

13. K. K. Kundu, Debabrata Jane, and M. N. Das, "Standard Potentials of Silver/Silver Iodide Electrode in Aqueous Mixtures of Ethylene Glycol at Different Temperatures and Thermodynamics of Transfer of Hydrogen Halides from Water to Glycolic Media," Electrochim. Acta (in press).

14. K. K. Kundu, A. L. De, and M. N. Das, "Solvent Effects on the Dissociation of Protonated Tris (Hydroxymethyl) aminomethane and p-Nitroanilinium Ion in Water-Ethylene Glycol Media at 25°C," J. Chem. Soc. (Perkin II), (in press).

15. K. K. Kundu, Debabrata Jana, and M. N. Das, "Studies in Some Isodielectric Media Part V, Standard Potentials of the Ag-AgCl Electrode in Methanol-Propylene Glycol Solvent System at Different Temperatures and Related Thermodynamic Quantities," Electrochim. Acta (accepted).

A.5.* STANDARD REFERENCE DATA

Project Title: POINT DEFECTS IN ALKALI HALIDES

Principal Investigator: Professor S. C. Jain

Institution: Indian Institute of Technology, Delhi

NBS Monitor: Dr. Lewis H. Gevantman

NBS Institute or Center and Division: Office of Associate Director for Information Programs; Office of Standard Reference Data

Summary Description of Project Goals

The purpose of this project is to collect, evaluate and compile critical tables of standard reference data on defect properties of non-metallic crystals.

Results and Implications to Date

The project started in 1968 with the aim of collecting and compiling a bibliography and also tabulating the critical tables of standard reference data on defects in alkali halides. The international journal literature is surveyed to collect the data. In addition, Physics Abstracts, Solid State Abstracts and Current Papers in Physics are reviewed to check on the thoroughness with which the pertinent literature is covered. A bibliography containing ~3000 references was published in 1971. By the end of 1971 the collection of the data on properties of defect centers in alkali halides was completed. The data have now been critically evaluated and the most reliable values compiled in the form of tables on "Electronic Absorption and Internal and External Vibrational Data of Atomic and Molecular Ions Doped in Alkali Halides." It is hoped that the tables will be published soon.

List of Publications that Resulted from the Project

1. S. C. Jain, S. A. Khan, H. K. Sehgal, V. K. Garg, and R. K. Jain, "Bibliography on Properties of Defect Centers in Alkali Halides," Report No. NBS-OSRDB-71-1, National Technical Information Service, Springfield, Virginia (Jan. 1971).

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

A.5.* STANDARD REFERENCE DATA

Project Title: REVIEW OF PHYSICAL PROPERTIES OF ALLOYS

Principal Investigator: Professor S. K. Joshi

Institution: University of Roorkee, Roorkee

NBS Monitor: Mr. Daniel Kahan

NBS Institute or Center and Division: Institute for Materials Research
Metallurgy Division

Summary Description of Project Goals

The aim of this project is to collect and critically evaluate experimental data for various alloys with particular emphasis on disordered phases. Theoretical interpretations of the evaluated data will be attempted. This work is to be done in support of and in close collaboration with NBS which is presently engaged in its Alloy Data Center in collecting, indexing and evaluating the large amount of published data on physical properties of alloys. This is a very large task for which assistance from expert groups in other countries is welcomed. India with a rapidly increasing technological and industrial involvement in complex alloys needs an awareness and detailed knowledge of the existence and availability of complex new materials and their behavior for specific applications and possible manufacture. This collaboration therefore can be of benefit to both parties involved and ultimately to world technology.

Results and Implications to Date

The project started in October 1972 with the object of compiling and critically assessing experimental data which are of major importance in the study of alloys. The principal investigator of the project has been entrusted with the task of reviewing the properties of alloys on the topics listed below:

1. Calculation of the electronic density of states.
2. Optical constants.
3. Specific heat.
4. Electrical conductivity.
5. Phonon frequencies.
6. Positron annihilation and Kohn effect measurements for Fermi surfaces.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

7. Order-disorder studies from x-ray and neutron diffraction.

8. Phase diagrams.

9. Superconductivity.

The NBS Alloy Data Center is already engaged in reviewing and evaluating the literature on Knight shift and soft x-ray spectroscopies. Nevertheless, these two areas will receive marginal attention in this project.

The investigator of the project has undertaken the responsibility of submitting periodically bibliographic compilations to the Alloy Data Center. Some of the material has already been dispatched and found to be suitable for incorporation in the base information available at that Center. It has also been possible to review the scheme of annotations used by the Data Center and suggest some modifications which have been approved as significant improvements.

List of Publications that Resulted from the Project

This project was started only recently and no publication has as yet resulted.

A.5.* STANDARD REFERENCE DATA

Project Title: PHYSICAL AND THERMODYNAMIC PROPERTIES OF HALOGENATED ALKANES

Principal Investigator: Dr. Arvind P. Kudchadker

Institution: Kanpur Critical Data Center, Indian Institute of Technology, Kanpur

NBS Monitor: Dr. Howard J. White, Jr.

NBS Institute or Center and Division: Office of Associate Director for Information Programs, Office of Standard Reference Data

Summary Description of Project Goals

The project involves an exhaustive literature survey, compilation, evaluation, selection, and correlation of physical and thermodynamic properties of bromo-, iodo-, and mixed fluorochlorobromoiodo alkanes. Refractive index, density, vapor pressure-boiling points, transition and freezing points, and critical constants are the physical properties investigated. The thermodynamic properties are also computed from the spectroscopic information. It is expected that this study will result in complete and detailed reports on most of the following: (1) bromo-, iodo- and mixed methanes; (2) Bromo-, Iodo- and mixed ethanes; (3) bromo-, iodo- and mixed higher alkanes; and (4) development of correlation techniques for the prediction of properties for which compounds, data are not available.

It is expected that some of the products of this Center will be sets of critically evaluated data which will contribute to the overall coverage of the thermodynamic and physical properties of organic compounds for the National Standard Reference Data System. In this task the Center will cooperate closely with the Thermodynamics Research Center at Texas A and M University which has similar tasks and with the Office of Standard Reference Data. Many classes of organic compounds are of great importance because of their widespread use in industry.

Results and Implications to Date

The project started in August 1970 with the purpose of collecting and compiling data from 1908 onwards through a detailed, systematic, and exhaustive literature survey on bromoiodo methanes. For each property, the collected data were arranged in chronological order for each compound and the compounds were arranged in standard order.

In this fashion summary sheets were prepared for the above mentioned properties. Then followed systematic and critical evaluation, and selection of "best" data for each

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

property and for each compound. Both graphical and computational techniques were used for this purpose. Various existing models were selected to fit the data for ease of interpolation and limited extrapolation. Out of a total of 69 halogenated methanes, reliable data on physical properties are available for about 15 compounds. The spectroscopic information is available for about 40 compounds. The available data on halomethanes have been arranged in tabular form to show the existence and the lack of data on properties for the compounds studied. This table is useful for the recommendation of needed future experimental work. Simultaneously, the literature survey was continued on haloethanes. The work completed by August 1972 is the following:

1. Literature survey, data compilation in the form of summary sheets, evaluation, selection, and correlation of the above mentioned properties for fluoro-, chloro-, bromo-, iodo-, substituted methanes.
2. Literature survey, data compilation in the form of summary sheets, and evaluation and selection on haloethanes.
3. Literature survey on vapor-pressure-boiling points, enthalpy of vaporization, virial coefficients, intermolecular forces, and P-V-T data for selected organic substances.

In addition to the publications mentioned in the subsequent section, the following manuscripts are in preparation:

1. S. A. Kudchadker and A.P. Kudchadker, "A Generalized Bond and Interaction Scheme for Thermodynamic Properties of Haloethanes."
2. V. K. Goyal and A.P. Kudchadker, "Vapor Pressure-Boiling Point Relationships - A New Vapor Pressure Equation."
3. P. R. Patnaik, P. P. Misra, Shukla, and A. P. Kudchadker, "Densities, Vapor Pressures, and Enthalpy of Vaporization of Halomethanes."
4. S. A. Kudchadker and A. P. Kudchadker, "Ideal Gas Thermodynamic Properties of Bromo- and Iodomethanes."
5. A. P. Kudchadker, "Virial Coefficients of Halomethanes."
6. S. A. Kudchadker and A. P. Kudchadker, "Enumeration of Substituted n-Alkanes."

List of Publications that Resulted from the Project

1. S. A. Kudchadker and A. P. Kudchadker, "Ideal Gas Thermodynamic Properties of Xenon Compounds," Proc. Indian Acad. Sci. 73, 261, Sec. A (1971).
2. A. P. Kudchadker, D. M. Agarwal, S. A. Kudchadker, "Ideal Gas Thermodynamic Properties of Chlorine, Bromine, and Iodine Pentafluorides," Indian J. of Chem. 9, 122 (1971).

A.5.* STANDARD REFERENCE DATA

Project Title: CRITICAL REVIEWS OF PHASE TRANSFORMATIONS IN INORGANIC SOLIDS

Principal Investigator: Professor C.N.R. Rao

Institution: Indian Institute of Technology, Kanpur

NBS Monitor: Dr. L. H. Gevantman

NBS Institute or Center and Division: Office of the Associate Director for Information Programs, Office of Standard Reference Data

Summary Description of Project Goals

Critical reviews were to be prepared in which thermodynamic, kinetic and other important data on phase transformations of inorganic solids were to be presented in an organized manner. The methods employed to study these transformations and changes in various properties accompanying the transformations were to be discussed. The reviews will be restricted to simple inorganic compounds such as chlorides, sulfates, nitrates, nitrites, carbonates, oxides, sulfides, and so on. Such reviews are expected to be of great value to chemists, physicists, materials scientists and others interested in the structure and properties of materials.

Results and Implications to Date

The following reviews have been undertaken and are in the indicated status:

1. Crystal Structure Transformations in Binary Halides, C.N.R. Rao and M. Natarajan, NSRDS Publication NBS 41, 1972.
2. Transition Metal Oxides, C.N.R. Rao and G.V. Subba Rao, NSRDS publication, in press.
3. Crystal Structure Transformations in inorganic carbonates, nitrates, and nitrites, C.N.R. Rao and B. Prakash. The first draft of this monograph is ready and will soon be submitted for publication.

Graduate and post doctoral students who are associated with the project have spent part of their time on research and have produced several publications based on experimental work associated with this project. Publications are listed below.

List of Publications that Resulted from the Project

1. M. Natarajan, B. Prakash, and C.N.R. Rao, "Defect Energies in CsCl and its Solid

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

Solutions with KCl, RbCl and CsBr," J. Chem. Soc. A, 1223 (1971).

2. C.N.R. Rao and M. Natarajan, "Crystal Structure Transformations in Binary Halides," NSRDS Publication NBS 41, 1972.
3. P. Ganguly and C.N.R. Rao, "Electron Transport Properties of Transition Metal Oxide Systems with the K_2NiF_4 Structure," Materials Research Bulletin (March 1973).

A.5.* STANDARD REFERENCE DATA

Project Title: INFRARED BIBLIOGRAPHY

Principal Investigator: Professor C.N.R. Rao

Institution: Indian Institute of Technology, Kanpur

NBS Monitor: Dr. L. H. Gevantman

NBS Institute or Center and Division: Office of the Associate Director for Information Programs, Office of Standard Reference Data

Summary Description of Project Goals

This project has been planned to prepare bibliographies of infrared spectroscopic data from the scientific literature. The material will be arranged on the basis of molecular formulae. For each compound, the empirical formula, chemical name and a list of references (author's names, journal reference) will be given; in addition, a brief description of the region covered and the nature of information available in each of the references will also be given. The material for the bibliographies will be taken from standard journals and will include all those publications which deal primarily with spectroscopy.

Results and Implications to Date

The first such bibliography has now been completed and is being typed.

List of Publications that Resulted from the Project

None

A.5* STANDARD REFERENCE DATA

Project Title: STUDIES OF METAL OXIDES, PHASE TRANSITIONS AND RELATED PROBLEMS

Principal Investigator: Professor C.N.R. Rao

Institution: Indian Institute of Technology, Kanpur

NBS Monitor: Mr. H. Steffen Peiser and Dr. H. F. McMurdie

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

Phase transitions and related studies on metal oxides and other inorganic solids were to be investigated. Some aspects of defect solids were also to be examined. The goals were adhered to. This project terminated in December 1971.

List of Publications that Resulted from the Project

1. A. K. Shukla, S. Ramdas, and C.N.R. Rao, "Intrinsic and Extrinsic Defect Pairs in Cesium Halides, J. Chem. Soc. Faraday II, 69, 207 (1973).
2. S. Ramdas, A. K. Shukla, and C.N.R. Rao, "Association Energies of Intrinsic and Extrinsic Defect Pairs in KCl," Chem. Phys. Letters, 16, 14 (1972).
3. C.N.R. Rao, S. Ramdas, R. E. Loehman, and J. M. Honig, "Semiconductor-Metal Transition in Ti_3O_5," J. Solid State Chem. 3, 83 (1971).
4. G. V. Subba Rao, P. N. Mehrotra, and C.N.R. Rao, "Semiconduction in Rare Earth Oxides," J. Solid State Chem., 2, 377 (1970).
5. M. Natarajan and C.N.R. Rao, "Phase Transitions in Silver Halides," J. Chem. Soc. (London), A, 3087 (1970).
6. C.N.R. Rao, G. V. Subba Rao, M. Natarajan, and R. E. Loehman, "Semiconductor-Metal Transitions in VO_2, NbO_2 and Some Solid Solutions of VO_2," J. Phys. Chem. Solids, 32, 1147 (1971).
7. G. V. Subba Rao, B. Wanklyn, and C.N.R. Rao, "Electrical Transport in Rare Earth Perovskites: Rare Earth Ortho -Chromites, -Manganites and -Ferrites," J. Phys. Chem. Solids, 32, 345 (1971).
8. G. V. Subba Rao, S. Ramdas, and C.N.R. Rao, "Electrical Conduction in Binary Oxides of the Type $M'O_2$-M''_2O_3," Indian J. Chem., 9, 242 (1971).

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

9. C.N.R. Rao, G. V. Subba Rao, and S. Ramdas, "Phase Transformations and Electrical Properties of Bi_2O_3," J. Phys. Chem., 73, 672 (1969).

10. C.N.R. Rao and K. J. Rao, "Phase Transformations in Solids," "Progress in Solid State Chemistry," Vol IV, Ed. by H. Reiss, Pergamon Press, Oxford (1967).

11. K. J. Rao and C.N.R. Rao, "Surface Energies of Alkali Halides," Indian J. Chem., 6, 637 (1968).

12. Schottky Defect Energies in Alkali Halides: Their Creation, Interaction and Migration," Physica stat solidi, 28, 157 (1968).

13. K. J. Rao and C.N.R. Rao, "Schottky Defect Energies in Cesium Chloride," Solid State Comm., 6, 45 (1968).

14. K. J. Rao, G. V. Subba Rao, and C.N.R. Rao, "Born Treatment of the Phase Transitions of Alkali Halides Employing New van der Waals Parameters," Proc. Phys. Soc. (London), 1, 1134 (1968).

15. C.N.R. Rao, M. Natarajan, and G.V. Chandrashekhar, "Heats of Crystallization of Amorphous Oxides," J. Chem. Eng. Data, 13, 235 (1968).

16. K. J. Rao and C.N.R. Rao, "Melting of Ionic Solids and the Born Treatment," Chem. Phys. Letters, 1, 499 (1968).

17. G.V. Chandrashekhar, P. N. Mehrotra, G. V. Subba Rao, and C.N.R. Rao, "Semiconduction of Non-Stoichiometric Rare Earth Oxides," Trans. Faraday Soc., 63, 1295 (1967).

18. G. V. Subba Rao, G.V. Chandrashekhar, and C.N.R. Rao, "Are Rare Earth Chromites Ferroelectric?" Solid State Comm., 6, 177 (1968).

19. K. J. Rao and C.N.R. Rao, "Pressure Transitions of Alkali Halides and the Born Treatment," Proc. Phys. Soc. (London), 91, 754 (1967).

20. K. J. Rao, G.V. Subba Rao, and C.N.R. Rao, "Pm3m-Fm3m Transformations of CsCl and its Solid Solutions with RbCl: Born-Meyer Treatment," Trans. Faraday Soc., 63, 1013 (1967).

21. P. N. Mehrotra, G.V. Chandrashekhar, E. C. Subbarao, and C.N.R. Rao, "Phase Transformations of Rare Earth Sesquioxides," Trans. Faraday Soc., 62, 3586 (1966).

22. K. J. Rao and C.N.R. Rao, "Crystal Structure Transformations of Alkali Sulphates, Nitrates and Related Substances: Thermal Hysteresis in Reversible Transformations," J. Materials Sci., 1, 238 (1966).

23. K. J. Rao and C.N.R. Rao, "Ferroelectric Transformation in KNO_2," British J. Appl. Phys., 17, 1653 (1966).

24. G. V. Subba Rao, M. Natarajan, and C.N.R. Rao, "Effect of Impurities on the Phase Transformation and Decompositions of $CaCO_3$," J. Am. Ceramic Soc., 51, 179 (1968).

25. M. Natarajan, T.S. Sharma, J. C. Ahluwalia, and C.N.R. Rao, "Thermal and Particle Size Effects on MgO," Trans. Faraday Soc., 65, 3088 (1969).

26. M. Natarajan, A.R. Das, and C.N.R. Rao, "Particle Size Effects and Thermal Hysteresis in Phase Transformations," Trans. Faraday Soc., 65, 3081 (1969).

27. M. Natarajan, K. J. Rao, and C.N.R. Rao, "Pm3m-Fm3m Transformations of Alkali Halides: Solid Solutions of CsCl with KCl, CsBr and $SrBr_2$," Trans. Faraday Soc., 66, 2497 (1970).

28. M. Natarajan, S. Ramdas, and C.N.R. Rao, "Antiferroelectric Transition in $CsPbCl_3$," Physics Letters, 29, 528 (1969).

29. S. Ramdas, K.C. Patil, and C.N.R. Rao, "Kinetics and Thermodynamics of Oxidation of Pr_2O_3 and Tb_2O_3 to Non-Stoichiometric Oxides," J. Chem. Soc. (London), (A), 64 (1970).

30. C.N.R. Rao and G.V. Subba Rao, "Electrical Conduction in Metal Oxides," Phys. stat. solidi, 1a, 597 (1970).

Ph.D. Theses (I.I.T.-Kanpur) of Research Fellows supported by NBS(G)-51

1. K.J. Rao, "Phase Transitions and Schottky Defects in Ionic Solids," Ph.D., (1967).
2. M. Natarajan, "Phase Transitions in Solids," Ph.D., (1970).
3. S. Ramdas, "Theoretical and Experimental Studies on Defect Solids," Ph.D. (1971).

A.5.* STANDARD REFERENCE DATA

Project Title: MAGNETIC PROPERTIES OF ATOMIC NUCLEI AND OF THE NUCLEAR ENVIRONMENT AND ON THE LIFETIMES OF NUCLEAR STATES

Principal Investigator: Dr. G. N. Rao

Institution: Indian Institute of Technology, Kanpur

NBS Monitor: Dr. Lewis H. Gevantman

NBS Institute or Center and Division: Office of Associate Director for Information Programs; Office of Standard Reference Data

Summary Description of Project Goals

The goals of the project are:

(a) To measure the hyperfine fields induced at nuclei due to electron polarization. These studies are expected to give better understanding of hyperfine interactions.

(b) To measure the lifetimes of nuclear excited states and to compare the experimental values with those predicted by the nuclear models. These studies enable us to understand the structure of these nuclei and also check the validity of the nuclear models.

(c) To prepare an up-to-date table of nuclear lifetimes and compare the evaluated values of the different multipole transitions with the predictions of the nuclear models.

(d) To prepare an up-to-date table of hyperfine fields and also to prepare an evaluated table for the dilute impurity hyperfine fields in host matrices of Fe, Co, Ni, and Gd.

Results and Implications to Date

(a) Hyperfine Field Studies

Dilute impurities embedded in ferromagnetic host matrices like Fe, Co, Ni, Gd etc. experience large internal fields. A general Hamiltonian of the impurity atom is quite complicated and therefore a formal solution of the impurity problem is difficult. Studies of the systematics [1][1] of these hyperfine fields as a function of the electronic configuration of the impurity resulted in useful

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

[1] Figures in square brackets indicate the publication reference at the end of this project review.

information about the possible mechanisms responsible for the electron polarization at the nucleus. So far we have measured the hyperfine fields on Sc in Fe, Re in Ni and Sc in Co, using the (γ-γ) perturbed angular correlation technique. These experimental values are compared with the existing models.

An automatic electromechanical Mössbauer system and a low temperature liquid helium cryostat were designed and fabricated. The Mössbauer apparatus will be used for the hyperfine field measurements in alloys.

(b) Nuclear Lifetime Measurements

Using the delayed coincidence techniques the short nuclear lifetimes in ^{44}Sc, ^{75}As, ^{99}Ru, ^{131}Cs, ^{133}Cs, ^{170}Yb, ^{181}Ta, ^{187}Re, and ^{197}Au were measured and compared with the predictions of the nuclear models.

(c) Nuclear Lifetimes Table

We have prepared a complete "Nuclear Lifetimes Table" wherein we have tabulated all the experimental values so far reported on the lifetimes of nuclear ground and excited states. All the data were processed with the help of a computer. Computer programs were developed to obtain the output with different options like increasing Z, increasing A, and increasing energy. Using this table another "nuclear lifetimes table" is being prepared with evaluated values. The evaluated values will be used for comparing the experimental transition rates with the single particle estimates. Comparisons with more realistic models are also planned.

(d) Table of Hyperfine Fields

A general table of hyperfine fields was prepared wherein all the values reported so far in the literature were tabulated. The data were processed with the help of a computer.

In order to study the systematics in general of the dilute impurity hyperfine fields in the host matrices of Fe, Co, Ni, and Gd all the experimental data available in the literature were collected and tabulated separately. Where multiple measurements exist, recommended or evaluated values were given. The impurity hyperfine field values plotted as a function of the electronic configuration of the impurity showed very definite and systematic trends.

These values are being compared with the existing models.

In addition to the publications mentioned in the following section, four papers are in an advanced stage of preparation:

1. "Nuclear Lifetimes Table" wherein all the values reported so far are listed. This will be brought out in a couple of months as a report of about 450 pages. The rough manuscript is ready.
2. "Evaluated Nuclear Lifetimes Table" wherein recommended values are given. This will be ready in a couple of months.
3. "Hyperfine Fields Table" wherein all the values reported so far are listed. The rough manuscript is ready and will be published soon.
4. "Dilute Impurity Hyperfine Fields" in Fe, Co, Ni, and Gd. Here the recommended values for the dilute impurities in the host matrices of Fe, Co, Ni, and Gd are given. The manuscript is ready and will be sent for publication soon.

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2. D. K. Gupta and G.N. Rao, "Nuclear Lifetime Measurements of Some Excited States in ^{75}As, ^{131}Cs, ^{133}Cs, ^{170}Yb, ^{187}Re, and ^{197}Au," Nucl. Phys. A182 669 (1972).
3. D. K. Gupta, A. K. Singhvi, D. N. Sanwal, and G. N. Rao, "Hyperfine Field Measurements on Sc in Fe and Re in Ni." Accepted for publication in Phys. Rev. B Solid State Physics, IIT, Technical Report No. 20/72.
4. A. K. Gupta, K. R. Sarma, J. J. Huntzicker, T. M. Srinivasan, and G. N. Rao, "Design and Fabrication of a Mössbauer Spectrometer and a Low Temperature Cryostat." Sent to Nucl. Instr. and Meth., IIT, also published as IIT, Technical Report No. 5/72.
5. A. K. Singhvi, D. K. Gupta and G. N. Rao, "Timing Properties of Ge(Li) Detector," accepted for publication in J. of Phys. Soc., Japan, Proc. of the Nucl. Phys. and Solid State Phys. Symposium, 555 (Feb. 1972).

6. A. K. Singhvi, D. K. Gupta, and G.N. Rao, "Hyperfine Field Measurements on Sc in Co," submitted for presentation at Nucl. Phys. and Solid State Phys. Symposium Dec. 1973 (to be published).
7. B. V. N. Rao, A. K. Singhvi, and G. N. Rao, "Decay of ^{49}Cr (41 min) and ^{189}W (11 min)," submitted for presentation at Nucl. Phys. and Solid State Phys. Symposium Dec. 1973 (to be published).
8. D. K. Gupta, D. N. Sanwal, and G. N. Rao, "Lifetime and Magnetic Moment of 68 KeV State in ^{44}Sc," Nuclear Phys. and Solid State Phys. Symposium (1971).
9. P. A. Narayana, T. M. Srinivasan, G. N. Rao, and P. Venkateswarlu, "Electron Paramagnetic Resonance Studies of Divalent Manganese in Ammonium Bromide Single Crystals," Nuclear Phys. and Solid State Phys. Symposium 1970 (to be published).

A.5.* STANDARD REFERENCE DATA

Project Title: INVESTIGATIONS ON MOLECULAR SPECTRA

Principal Investigator: Professor Nand Lal Singh

Institution: Banaras Hindu University, Varanasi

NBS Monitor: Dr. A. Bass

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

This scheme was undertaken with a view to investigate the spectra of diatomic and polyatomic molecules in the visible, near ultraviolet, and near infrared regions.

Results and Implications to Date

The NBS PL-480 grant provided for the scheme has generally added greatly to the facilities and scope of the Laboratory. The grant received has been utilized in designing and constructing appropriate sources for emission of radiation and in procuring some useful instruments which could not have been procured through normal grants.
The facilities that have been created greatly assist in furthering research and training programs. Fellowships have been awarded to several research scholars who have secured Ph.D. degrees.

1. Rotational and Vibrational Structure of the Electronic Spectra of Diatomic Molecules:

Extensive studies have been made in the structure of electronic spectra of diatomic molecules using a 35 ft. concave grating spectrograph. Ran B. Singh, B.S. Mohanty, K.N. Upadhya, D. K. Rai, and N. L. Singh studied the rotational structure of PO β-system from plates taken on 35 ft. grating spectrograph. These studies have resulted in accurate determination of rotational and vibrational constants for the $B^2\Sigma$ and $X^2\Pi$ states in the PO molecule. The peculiar feature of reversal of shading in these bands has been explained. The calculation of the Franck-Condon factors and the potential energy curves for several states have been accomplished.

The rotational analyses of the B-X system of ^{121}SbO and ^{123}SbO have been made more accurately than before by Ran B. Singh and K.N. Upadhya. The isotope effect has been detected for the first time in the spectra of this molecule. The D-X system in the spectrum of SbO has also been analyzed.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

Studies of the electronic spectra of BiCl and BiF have been carried out in great detail. The rotational analyses of the A-X systems of the two molecules have been extended and the A'-X system of BiCl and C-X systems of BiF have been analyzed for the first time.

The analysis of the C-X system of BiF given by B. S. Mohanty and A. K. Choudhary involves forbidden transitions from (a)^3¶ to singlet lower states.

The analysis of the rotational structure of A-X and B-X systems of CaF is also new and though large spin doubling and small sequence separations made the analyses quite difficult, useful constants have been derived. The isotope effect has been used to reanalyze the vibrational structure of the SrCl bands.

2. Investigations of Electronic and Vibrational Spectra of Substituted Benzenes:

The number of molecules studied under this heading is too large to be enumerated. The results obtained are backed by data which have formed the basis of several publications listed below. We have succeeded in analyzing the vibrational structure in the electronic spectrum of several such molecules. One interesting aspect of these studies has been the study of the emission spectra in the presence of flowing vapor of benzene. In several cases this has resulted in the excitation of singlet-triplet transitions in the vapor phase, which is well-nigh impossible otherwise. Another interesting investigation has been the study of hydrogen bonding in derivatives of quinone.

A new line of investigation was started by Dr. S.N. Thakur who studied the absportion spectra of several para fluorinated benzenes under the high resolution obtainable in the third order from the 35 ft. grating. He succeeded in resolving the K-structure. This structure was analyzed on the basis of the symmetric top approximation and thus yielded approximate rotational constants for the upper electronic state. The accuracy of measurement of the structure has been very recently demonstrated clearly by more detailed calculations of Dr. Hollas of Reading University, England.

In this project the Indian group succeeded in making some contributions to a basic aim of the National Bureau of Standards; providing reliable data for science and technology. The NBS project monitor, Dr. A. M. Bass, has been examiner of some of the Ph.D. theses from this Laboratory.

List of Publications that Resulted from the Project

Although this project was operative only from 1963 to 1968 inclusive, the output of results and scientific publication continued well beyond the formal termination of the grant. (Only a partial list is here given because of the large number of publications.)

Spectra and Structure of Diatomic Molecules

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A.5.* STANDARD REFERENCE DATA

Project Title: THE INVESTIGATION OF THE DECAY OF EVEN-EVEN NUCLEI IN THE MEDIUM WEIGHT REGION

Principal Investigator: Professor P. N. Trehan

Institution: Panjab University, Chandigarh

NBS Monitor: Dr. R. S. Caswell

NBS Institute or Center and Division: Institute for Basic Standards
Center for Radiation Research

Summary Description of Project Goals

In the medium atomic weight range the behavior of the energy levels of the nuclei with even numbers of protons and neutrons is characterized by a vibration like sequence of levels with spins of 0^+, 2^+, or 4^+ for the second excited state. The ratio of the energies of the second to the first excited state lies between 1.8 and 2.5.

It was proposed to investigate such behavior in detail for certain medium-weight and even-even nuclei. This project meant setting up the following well known facilities for nuclear spectrometry:

1. Single-crystal spectrometer
2. Gamma-gamma and beta-gamma scintillation spectrometer
3. Angular correlation table
4. Sum spectrometer
5. Coincidence sum spectrometer (Hoogenboom type)
6. Beta-ray magnetic spectrometer

The measurements with some of this equipment would permit the measurement of the frequency and intensity of the various radiations observed in the decay of a nuclide under investigation and in turn help in the clarification of the relevant decay scheme.

The gamma-gamma angular correlation studies, wherever possible, would give the value of δ, the mixing ratio of E2 and M1 for the cascade transition from the second 2^+ level. This value of δ can also be obtained from the magnetic spectrometer measurements of the K-conversion co-efficient and the K/L ratio. The value of δ can then be compared with the value expected from the theory by Davydov and Fillippov.

The value of δ and the ratio of the crossover-to-cascade for the second 2^+ level obtained from our measurements would give the ratio of the reduced transition probability for this level. This ratio can then be compared with the theoretically expected value from

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

the various models.

From the final proposed decay scheme one can obtain the log ft. values (measures of decay probabilities) for the various beta or electron conversion transitions. Also the multipolarities of the various gamma rays could be obtained from conversion coefficient measurements, and these would enable suitable spin and parity assignments to be made to the various levels of the nucleus.

Results and Implications to Date

The decay of a number of nuclei such as ^{99}Mo, ^{103}Ru, ^{110m}Ag, ^{124}Sb, ^{131}Ba, ^{131}I, ^{133}Ba, ^{134}Cs, ^{144}Ce, ^{144}Pr, ^{160}Dy, ^{182}Ta, ^{192}Ir, and other nuclei have been investigated during the last six years of the project. For these investigations, a single crystal scintillation spectrometer, a slow-fast coincidence setup, a modified sum-coincidence spectrometer, and a sum-peak coincidence spectrometer have been utilized. The detectors employed were two pairs of Harshaw's integral line assemblies containing 2" x 2" and 3" x 3" NaI(Tl) crystals having good energy resolutions. Thin NaI(Tl) crystals were also used. Recently a Ge(Li) detector has been used for our investigations. The energies, relative intensities and coincidence relations of various gamma rays emitted in the decay of the nuclei under study were carefully measured. In general, wherever very weak gamma rays or multiple gamma ray cascades were involved the modified sum-coincidence and sum-peak coincidence spectrometers have been found very useful, because in the former the degraded photons are not registered and in the latter the coincidence detection efficiency is very high, especially when used in 3π or 4π geometries. In addition, gamma-gamma angular correlation studies have been made using the fast-slow coincidence setup. In some cases, the sum-peak coincidence spectrometer has been utilized with advantage for this purpose. Internal conversion coefficient measurements have also been made in a limited number of transitions in some of the nuclei.

From our measurements, it has been possible to decide about the existence, intensity, and position of some of the low intensity gamma rays in some of the nuclei. The value of δ obtained in some cases have been compared with the values obtained from suitable nuclear models. Interesting results bearing upon the applicability of such models have been obtained.

From the cross over-to-cascade ratios and the measured δ values, the reduced transition probabilities have been obtained. These results, when compared with single particle estimates, have yielded information about the nature of some of the levels.

The multipolarities of a large number of gamma rays have been determined from our measures δ values and conversion coefficients (either measured or taken from literature). This has enabled us to assign spin and parity to various levels of the above mentioned nuclei. In some cases, the measured level structures were compared with the level structures predicted by some nuclear models.

In addition to the above studies, theoretical neutron inelastic scattering cross-section calculations have been made for a few levels in ^{115}In, ^{127}I, and ^{197}Au using the Hauser Feshbach method and a suitable optical model potential. The results have been compared with the measured level excitation cross-sections. Spin-parity assignments have been made to these levels on the basis of these comparisons.

The data on ^{56}Fe (p, p'γ) reaction taken at Bartol Research Foundation, Swarthmore, Pennsylvania, were analyzed. The experimental cross-sections of the various levels and the angular distribution of the various gamma rays in ^{56}Fe were obtained from this analysis. Theoretical calculations for the level cross-sections and the angular distributions were made using Moldauer's theory and a suitable optical model potential. Theoretical results when compared with experimental results yielded spin assignments to a number of levels of ^{56}Fe excited in this reaction.

With the recently acquired Ge(Li) detector and a transistorized multi-channel analyzer, it has been possible to measure energies of gamma rays emitted in the decay of ^{131}I to a precision of 0.1 to 0.2 %. We have been able to measure also the intensities of gamma rays with much greater precision than hitherto possible.

The NBS/SFCP (PL 480) has provided research facilities to train many students in the field of nuclear physics, and enabled us to provide some new information in the field of nuclear physics.

The NBS monitor points out that nuclear decay scheme information is becoming increasingly important to such fields as nuclear medicine, environmental protection, clean nuclear energy as well as to basic science.

List of Publications that Resulted from the Project

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A.5.[*] STANDARD REFERENCE DATA

Project Title: OPTICAL SPECTRA OF SIMPLE MOLECULES

Principal Investigators: Professors Putcha Venkateswarlu
Professor D. Ramachandra Rao

Institution: Indian Institute of Technology, Kanpur

NBS Monitor: Dr. Arnold Bass

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

An attempt will be made to measure the spectra of excited halogens and mixed halogens trapped in argon matrix and to understand the effect of crystal fields. Single crystals of alkali halides and nitrates will be grown with impurities like OH^-, O_2^-, CN^-, NO_2^- and VO^{2+} and their optical spectra will be studied to understand the solid state effects on the energy levels of these ions.

Sealed tube techniques and microwave excitation will be utilized in search of new free radicals formed by the combination of the elements in group VI. High resolution spectra of such molecules will be studied in order to obtain spin orbit coupling strengths and the order of electronic configurations. Isotopically enriched samples will be used.

Emission spectra of iodine, bromine and chlorine will be recorded in the near infrared and visible regions in order to study the band systems of these molecules and their ions. These systems will also be looked into under high resolution. Attempts will be made to obtain iodine molecular lasers in the predicted regions of 4400-4000 and 3500-3000Å. During the experiments on the emission spectra of halogens in the near infrared, attempts will be made to obtain lasing action in this region also.

A study of thermal luminescence of I_2, Br_2 and Cl_2 in presence of argon will be taken up to try to understand the relaxation mechanism in the $^3\pi_{o\,u}^{\;\,+}$ and $^3\pi_{1\,u}$ states as well as the formulation of these states. Further a study of I_2 absorption at different temperatures up to 1400°C will be attempted at high resolution together with juxtaposed emission spectra in an effort to understand the correlation of absorption and emission in this region.

The NBS monitor states that from his viewpoint the Indian work is related to activities in the Physical Chemistry Division that are concerned with problems of molecular structure

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[*] The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

and energy transfer in excited molecular states. These data are important for understanding relaxation processes and chemical kinetics of halogen-containing species.

Results and Implications to Date

The necessary vacuum systems have been fabricated for the excitation of halogens. The vacuum systems that are constructed can simultaneously be used for possible laser action by employing appropriate mirror.

Work has started on I_2. In our preliminary experiments, in certain types of electric discharge through iodine vapor, a number of main bands are observed in the region between 6700-9000 Å . The spectra also show a large number of weak bands slightly diffuse. Some of these bands appear to be the counter parts of the absorption band system already recorded in literature. More intense investigation in this region of spectrum has been undertaken.

Spectra have been recorded under the following three conditions of discharge:

1. 9000V, DC discharge through iodine vapor
2. Microwave discharge (2450MHz) through iodine vapor in the same condition as above.
3. 12000 AC transformer discharge through iodine vapor

Results so far obtained indicate that the first two types of discharge give relatively large number of atomic lines of iodine and are, therefore, not suitable for the production of molecule bands. The third method of excitation has given a good number of fairly sharp bands in the region between 5400 and 8900 Å. The spectra have been photographed on 1.4 meter Jarrell Ash f/6.3 spectrograph.

The spectrum produced by the AC discharge has been measured and the wave lengths of the bands recorded. The absorption spectrum of the iodine vapor in the above discharge tube has also been mapped employing a tungsten filament lamp as the continuous source. Most of the bands obtained in absorption seem to be identical with the bands in emission. Analysis of the bands is in progress.

Similar work on bromine and chlorine is about to start.

The spectra of ^{15}N ^{78}Se and ^{15}N ^{80}Se molecular species have been excited in microwave discharge (2450MHZ) and photographed in the third order of a 3.4 meter Jarrell Ash spectrograph with a 30000 lines/inch grating. The analysis of the spectrum gives the following molecular constants for the two brand systems studied:

$^{2}\pi_{3/2} - {}^{2}\pi_{3/2}$ System, $\nu_e = 23901.50\ \text{cm}^{-1}$

Molecular Constant	$^{15}N\ ^{78}Se$ (cm^{-1})	$^{15}N\ ^{80}Se$ (cm^{-1})
W''_e	929.68	927.80
$W''_e\nu_e$	5.41	5.39
B''_1	0.5061	0.5039
B''_2	0.4820	0.4806
B''_3	0.4785	0.4765
B''_4	0.4760	0.4726
B''_5	0.4716	0.4672
D''_e	5.85×10^{-7}	6.00×10^{-7}
W^1_e	683.36	681.98
$W^1_e\nu_e$	42.39	42.20
B^1_o	0.3955	0.3938
B^1_1	0.4020	0.3985

$^{2}\pi_{1/2} - X\ ^{2}\pi_{1/2}$ system, $\nu_e = 24357.12\ \text{cm}^{-1}$

Molecular Constants	$^{15}N\ ^{78}Se$ (cm^{-1})	$^{15}N\ ^{80}Se$ (cm^{-1})
W_e''	932.44	930.52
$W_e''\nu_e''$	5.47	5.45
B_3''	0.4774	0.4766
B_4''	0.4746	0.4725
B_5''	0.4707	0.4625
D_e''	$0.5\text{x}10^{-6}$	$0.5\text{x}10^{-6}$
W_e''	635.01	633.73
B_o^1	0.3900	0.3885
D_e^1	$0.5\text{x}10^{-6}$	$0.5\text{x}10^{-6}$

List of Publications that Resulted from the Project

The project has only recently been undertaken and no substantial publications have emerged so far.

A.6.* STANDARD REFERENCE MATERIALS

Project Title: PREPARATION OF STANDARD REFERENCE MATERIALS OF FERRO-ALLOYS

Principal Investigator: Professor V.A. Altekar
Associate Investigator: Dr. H. P. Bhattacharya

Institution: National Metallurgical Laboratory, Jamshedpur

NBS Monitor: Dr. R. E. Michaelis

NBS Institute or Center and Division: Institute for Materials Research
Office of Standard Reference Materials

Summary Description of Project Goals

This project involves the preparation, homogeneity testing, and analysis of three ferro-alloys for use as NBS Standard Reference Materials in the following order of priority:

1. High-carbon Ferromanganese,
2. Low-carbon Ferromanganese, and
3. Ferrotitanium

The crushing, grinding, mixing and sampling operations on 1/2 to 1 ton lots of the materials will be undertaken initially, followed by chemical analyses of various sieve fractions to establish the homogeneity. The ferro-alloys should conform to ASTM specifications A99 Grade A, A99 Grade A (low carbon), and 324 Grade B respectively.

The NBS distributes standard reference materials including those of ferroalloys used by the steel industry throughout the world for the control of raw materials. Any help in the preparation of these critical materials is clearly welcomed by NBS. From the point of view of National Metallurgical Laboratory in India, the participation in this demanding work increases the self confidence and credibility of NML in supplying these materials to indigenous industry, as required by such industry.

Results and Implications to Date

The NBS monitor states that from his viewpoint the Indian work on the preparation, testing, and certification of important ferroalloys has been performed in an outstanding manner. NBS currently is involved in the preparation of two additional ferroalloys, specifically regular and high purity grade 75% silicon. This work also has international ramifications in that the Bundesanstalt für Materialprufung (BAM) in Germany is cooperating

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

with NBS on this program. It has now been a number of years since NBS has had ferromanganese and ferrotitanium materials available, and therefore, the India project on these ferroalloys highly complement and support the NBS program for maintaining a continuous supply of important steelmaking alloys.

High carbon ferro-manganese

A suitable sample of high carbon ferro-manganese, fairly within the ASTM specifications was received from M/s. Ferro Alloy Corporation Ltd., India and one ton of the raw material was thereafter obtained from this firm. Systematic studies on various sieve fractions of a representative sample taken from the bulk lot of one ton showed that -60 + 100 BSS mesh size would be most suitable for preparation of this category of standard sample conforming to the suggested ASTM specifications. The bulk sample of 1000 kg was divided into two lots and for each lot crushing, grinding, and homogenizing operations were carried out separately in different batches and a total of 280 kg of standard sample was finally prepared.

ASTM A99 Grade A(High C) Specification	Element	Analysis of NML SRM
78.00% Min	Mn	80.9%
0.35% Max	P	0.183%
0.05% Max	S	Trace
1.20% Max	Si	1.14%
7.50% Max	C	6.77%

Low carbon ferro-manganese

Out of the two samples of low carbon ferro-manganese, the one received from M/s. Electro Metallurgical Works, Bombay, was found to be of proper grade. An order was, therefore, placed for a supply of 500 kg of the material and against this only 380 kg of raw material was received. Systematic crushing, grinding, and homogenizing operations on the 380 kg of the material were carried out in different batches and 117 kg of the fraction of -60 + 100 BSS mesh size was finally obtained, an analysis of which is given below:

ASTM A99 Grade A(Low C) Specification	Element	Analysis of NML SRM
85 - 90 %	Mn	85.6%
0.07 - 0.5%	C	0.12%
2 - 00% Max	Si	1.73%
0.20% Max	P	0.118%
0.20% Max	S	Trace

Ferro-titanium

Procurement of ferro-titanium conforming to the standard specifications took the longest time. It was indeed difficult to obtain 500 kg of the material conforming to our specifications made in one melt as per direction. Ultimately, after a good number of experimental trials by the producers, a 500 kg lot of the raw material conforming to the specifications was received from M/s. Indian Thermit Corporation Ltd., Kanpur. The sieve fraction selected was -60 + 100 BSS mesh size. Crushing, grinding, and homogenizing operations were carried out in different batches. The final sample after homogenizing weighed 175 kg. The analytical data of the final sample are shown below:

ASTM 324 Grade B Specification	Element	Analysis of NML SRM
20 - 27%	Ti	24.98%
5.0% Max	Si	2.31%
6.0% Max	Al	5.64%
0.1% Max	C	0.048%

It is hoped that these series of experiments which the NML has undertaken will be fruitful in scientific activities of the NBS and will provide a great help to the ferro-alloy industries in rapid and accurate analyses of the raw materials and finished products in both countries. A suitable portion of the high carbon ferro manganese will be immediately sent to NBS for confirmative analytical tests and homogeneity appraisal. Plans will then be made how to handle the other SRM's.

List of Publications that Resulted from the Project

This project has only recently been executed. When the NBS results on the SRM's are available a literature publication may become desirable. The Journal of Research of the National Bureau of Standards would be a good medium.

A.6.* STANDARD REFERENCE MATERIALS

Project Title: GLASS AND CERAMIC CHEMICAL COMPOSITION - SRM PROGRAM

Principal Investigator: Dr. S. Kumar

Institution: Central Glass and Ceramic Research Institute, Calcutta

NBS Monitor: Dr. Oscar Menis

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

The project was to involve complete analyses of glass and ceramic materials as part of the standard reference materials (SRM) program. It also was to include the development and standardization of analytical methods for the determination of constituents for which existing analytical methods cannot be satisfactorily applied.

Results and Implications to Date

Four SRM samples (two clays and two feldspars) were analyzed in triplicate by independent procedures after proper standardization. The constituents determined were SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, P_2O_5, BaO, Na_2O, and K_2O.

While analyzing SRM samples, it was found that analytical methods available in the literature for certain constituents could not be satisfactorily applied to SRM samples, and in such cases, investigations were carried out for the development of suitable methods or modifications of existing ones. For example, the colorimetric determination of titanium using hydrogen peroxide was not sufficiently sensitive in the range of 0.004-0.006% TiO_2. Critical studies were carried out on the spectrophotometric determination of titanium using chromotropic acid as the chromogenic reagent. The results of the investigation are being prepared for publication.

The existing procedures for the colorimetric determination of residual silica by the molybdenum blue method were also carefully studied and it was observed that the experimental conditions were not properly defined to ensure reproducible results. In view of this, further investigations were carried out on this method and a satisfactory procedure was developed uing ascorbic acid as the reducing agent.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

The present collaborative work provided the opportunity to check the precision of some of the analytical methods that were developed or standardized in the Indian Laboratory and to augment existing competence for such accurate analyses.

In a letter dated September 11, 1971 to Dr. Kumar, the monitor stated that "we are pleased to report that, in general, your values are in very good agreement with provisional values established for these four standards. As you know, feldspars and clays are very complex materials which require considerable analytical skill. You and your associates are to be complimented for the fine work which resulted from this cooperative program." Thus, the NBS monitor states that from his viewpoint the Indian work provided valuable analytical information on a number of complex SRM's which required considerable analytical skill and experience.

Two publications of this work at the Central Glass and Ceramic Research Institute are being prepared. One of these being communicated to the Analyst, London is by B.C. Sinha and S. Dasgupta, entitled "Spectrophotometric Determination of Silicon by the Heteropoly Blue Method."

List of Publications that Resulted from the Project

None to date.

Project Title: LOW TEMPERATURE AND HIGH PRESSURE X-RAY INVESTIGATIONS OF PHASE TRANSITIONS

Principal Investigator: Dr. K. V. Krishna Rao

Institution: Osmania University, Hyderabad

NBS Monitor: Dr. Stanley Block

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

In the past, X-ray investigations on the thermal behavior of a number of crystals of rutile [1][1] and calcite [2, 3, 4, and 5] type structures have been undertaken. Studies on the thermal expansion of many crystals belonging to the same crystal type are useful in correlating the thermal expansion with other physical properties and parameters, such as bond lengths and percentages of ionic character. Other interesting results obtained are the negative coefficients of expansion along the unique axis in the case of FeF_2, CrO_2, and RuO_2. These studies have also been extended to single crystals [6] at low temperatures. In a few cases the crystal structure has been refined to determine the B factors for different atoms with a view to correlating the thermal expansion with the thermal vibrations [7]. The objectives of the present project are:

(1) to study the phase transitions, crystal structure, and the thermal expansion of organic and inorganic compounds at low and high temperatures;

(2) to study the thermal expansion and structure of organic and inorganic crystals at room and low temperatures; and

(3) to study the phase transitions of organic and inorganic crystals under high pressure,

with special stress on rutile, calcite, and K_2SO_4 type compounds.

Results and Implications to Date

Although the official commencement of the project was September 23, 1971, there was considerable delay in receiving the grant and the staff for the scheme was recruited only in March 1972 when the actual work on the project commenced. The following is the progress

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

[1] Figures in square brackets indicate the publication reference at the end of this project review.

made so far.

(a) Studies on Thermal Expansion

The lattice parameters of two ferrites, cobalt ferrite ($CoFe_2O_4$) and cobalt-zinc ferrite ($Co_{0.2}Zn_{0.8}Fe_2O_4$) have been determined in the temperature range 30°C to 700°C to ascertain whether there are discontinuities in the variation of the lattice parameters at the Curie temperature. It has been noticed that there is no abnormality in the vicinity of the Curie temperature in either of the compounds. The coefficients of thermal expansion at different temperatures have been evaluated using a graphical method.

(b) Determination of Crystal Structures

To determine the crystal structure of α - (phenyl sulphonyl)-chalcone, $C_{21}H_{26}O_3S$, whose space group has already been determined in this laboratory [8], intensity data on 700 reflections have been collected by the photographic method from Weissenberg photographs. The structure determination of this substance is in progress.

A physiologically active compound bromohypophyllanthin $C_{24}H_{28}O_7Br_2$ is also taken up for investigation. The space group and the unit cell dimensions have been determined from the rotation and Weissenberg photographs. The intensity data are being collected.

(c) High Pressure Studies

An MRC high-pressure high-temperature X-ray camera has been set up. The first substance taken up for investigation is potassium nitrate, whose thermal behavior has already been studied in this laboratory [7]. X-ray powder photographs at atmospheric pressure and pressures of approximately 8 kb and 12 kb have been recorded. The analysis of these photographs is in progress.

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List of Publications that Resulted from the Project

Two publications are under preparation.

A.8.* MATERIALS MEASUREMENT METHODS AND STANDARDS

Project Title: CATALYTIC HIGH PRESSURE HYDROGEN TRANSFER REACTIONS

Principal Investigators: Dr. C. N. Pillai
Dr. M. Satyanarayana

Institution: Indian Institute of Technology, Madras

NBS Monitor: Dr. Ralph Klein

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

The objective of the work is to study the catalytic hydrogenation of aromatic compounds under pressure by hydrogen transfer from suitable hydrogen donors. The work will involve the development of catalysts, a study of reaction mechanisms, the development of the reaction as a synthetic tool in organic chemistry, and a further detailed study of suitable reactions from the technological point of view.

Results and Implications to Date

The project was activated only very recently; results are therefore as yet unavailable.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

A.8.* MATERIALS MEASUREMENT METHODS AND STANDARDS

Project Title: STUDY OF TRANSITION METAL OXIDES WITH SPECIAL REFERENCE TO THEIR CATALYTIC PROPERTIES

Principal Investigators: Professor M.V.C. Sastri
Professor V. Srinivasan

Institution: Indian Institute of Technology, Madras

NBS Monitor: Dr. Ralph Klein

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

In the project it is envisaged to carry out a comprehensive investigation of the preparation, solid state properties, and catalytic behavior of binary and ternary oxides of a wide range of transition metals.

The NBS monitor states that because of the extensive work of the NBS Surface Chemistry Section on adsorption, surface migration, surface reactions, and surface energies, the interests of NBS have been very close to catalysis. The Indian work embodied in this project is an extension of the work on surfaces, bridging the effort of NBS with industrial applications. Since NBS has become more interested and involved with catalysis, the work at IIT Madras is a natural complement of the clean surface work at NBS.

Results and Implications to Date

The work carried out under this project since its commencement in September 1970 to date is summarized below in two parts: I. Preparation and solid state chemistry of the complex oxides and II. Catalytic reaction studies thereon.

I. Preparation and solid state chemistry of complex oxides

(a) Mixed oxides of V and Zr experiments with the "precursor" method:

Two general methods are available for the preparation of complex (ternary) metal oxides: (1) Solid state reactions between the respective oxides of the metals or between their carbonates and oxides; and (2) The so-called "precursor" method [1][1] involving essentially heating a complex compound of easily decomposable anions, such as carbonates, oxalates and formates of the metal ions concerned; eg., Ba $[TiO(C_2O_4)_2]$ and Tl $UO_2(H\,COO)_3$. The former method generally requires prolonged heating at rather

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

[1] Figures in square brackets indicate the publication reference at the end of this project review.

high temperatures (900 to 1500°C). The difficulties inherent in the control of experimental parameters under such conditions are reflected in uncertainties in the purity, homogeneity, and stoichiometric reproducibility of the products. The precursor method, on the other hand, requires less exacting conditions and consequently has greater promise of yielding products of desired composition and homogeneity. It was therefore considered worthwhile to explore the possibilities and potentialities of the precursor method for the preparation of the complex oxides of transition metals as one of the important subsidiary goals of the project. During the period under review the method was successfully employed for the preparation of complex oxides of vanadium and zirconium from oxalate-precursors of the compositions:

$M_3[VO_2(C_2O_4)_2].6H_2O$ and $M[VO(C_2O_4)_2].n\,H_2O$

where M = Ba (II) or Sr (II). The thermal behavior of these compounds were studied by the Differential Thermal Analysis and the Thermogravimetric methods. Mixed metal oxides obtained as final products of decomposition were characterized by x-ray diffraction, magnetic susceptibility and electrical conductivity measurements. It was found that decomposition in air resulted in pentavalent vanadium oxides, $Ba_3V_2O_8$, $Ba_2V_2O_7$ and $Sr_2V_2O_7$, while decomposition in flowing nitrogen or in vacuum (ca.10^{-2} Torr) yielded mixed tetravalent and/or trivalent vanadium (III) oxides. Perovskite type $BaVO_3$ obtained by the thermal decomposition of the corresponding complex oxalate in oxygen-free nitrogen atmosphere has a 4H-polytypic structure in contrast with those of other alkaline earth metal vanadates (IV), $CaVO_3$ and $SrVO_3$ which crystallize in a regular perovskite structure [2]. The corresponding strontium compound prepared by similar method was found to possess an anion deficient pervoskite structure, $SrVO_{2.75}$.

Perovskite type zirconates, $AZrO_3$, (A = Ca, Sr, Ba, and Pb) have also been prepared by the precursor method. Textraoxalato zirconates (IV) of the general composition $A_2[Zr(C_2O_4)_4].xH_2O$ were employed as the precursors. ZrO_2 in cubic form has been obtained by a similar method from the corresponding ammonium compound.

In an attempt to prepare lower vanadium oxides, the thermal decomposition of $VOC_2O_4.2H_2O$ and $(NH_4)_2[VO(C_2O_4)_2].3H_2O$ have been carried out under low pressure (ca.10^{-2} Torr) conditions. Both the compounds yield V_2O_3 as the final product.

In an attempt to prepare lower vanadium oxides, the thermal decomposition of $VOC_2O_4 \cdot 2H_2O$ and $(NH_4)_2 [VO(C_2O_4)_2] \cdot 3H_2O$ have been carried out under low pressure (ca.10^{-2} Torr) conditions. Both the compounds yield V_2O_3 as the final product.

The thermal decomposition of NH_4VO_3 and the reduction of V_2O_5 in flowing hydrogen atmosphere has been investigated by DTA to see if V_2O_3 and VO_2 were formed. NH_4VO_3 decomposes endothermally around 200-210°C to yield an ammonium vanadium "bronze" $(NH_4)_x V_2O_5$. The latter undergoes further reduction exothermally around 480° to yield V_2O_3.

In view of the importance of divalent transition metal vanadates (V) as catalyst materials, a comprehensive study of both solid state chemistry and catalytic aspects of such vanadates has been undertaken. The preparation, dehydration, and transformation [3] of $Co(VO_3)_2 \cdot 2H_2O$ have been studied using DTA, infrared spectroscopy (IR), and X-ray diffraction (XRD) methods.

(b) Ferrites:

Ferrites, AFe_2O_4, with spinel structure, are of technical importance in view of their ferrimagnetic [4] and catalytic [5] properties. The corresponding chromites are also gaining importance because of their useful catalytic and ceramic properties [6]. With a view to understanding the mechanism and the factors controlling the formation of such compounds, the formation of $ZnFe_2O_4$ and $NiCr_2O_4$ from the constituent oxides has been studied. It is found that the lowering of oxygen pressure in the ambient atmosphere favors ferrite formation while oxygen pressure has no effect on chromite formation. Both the reactions follow a mechanism involving diffusion of cations.

(c) Mixes oxides of manganese and molybdenum:

Transition metal oxides featuring molybdenum have come into considerable prominence as catalyst materials for a variety of reactions, such as oxidation, dehydration, and dehydrogenation of organic compounds. Since the catalytic and solid state properties are generally related, a detailed study of complex oxides found in the system Mn-Mo-O was undertaken. Three important stoichiometric compositions are known in the system: $MnMoO_4$, Mn_2MO_6, and $Mn_2Mo_3O_8$. $MnMoO_4$ can be obtained by interaction of either $MnCO_3$ and MoO_3 or MnO_2 and MnO_3. Studies carried out by TGA and effluent gas analysis (EGA) methods, reveal that the decomposition of $MnCO_3$ precedes the formation of $MnMoO_4$. The kinetic rate data for the reactions between $MnCO_3$-MoO_3 and MnO_2-MoO_3 have been analyzed on the basis of various rate equations for solid state reactions. It has been found that the former reaction is best described by the Kroger-Ziegler model, while the latter follows Jander's model. The DTA study of the reactions in N_2 atmosphere reveals that Mn_2O_3 is the main reactive species in the reaction. Marker studies of the reaction between pellets of MnO_2 and MoO_3 in air indicate that Mn^{2+} is the main diffusing species.

II. Studies on catalysis by mixed oxides

(a) Dehydrogenation of cyclohexane and cyclohexene on zinc molybdate catalysts:

Two samples of zinc molybdate catalysts were prepared, one by solid state reaction between ZnO and MoO_3 and the other by co-precipitation as hydroxides from zinc nitrate and ammonium paramolybdate. Both these catalysts promoted the dehydrogenation of cyclohexane and cyclohexene which could be associated with the Mo-O Π - ← bond character. The actual oxidation state of the cations under reaction conditions was identified by electron spin resonance (ESR) spectroscopy and it was found that a paramagnetic species ($g = 1.9221$) (probably Mo^{5+}) is the active species involved in the dehydrogenation reaction.

(b) Decomposition of isopropyl alcohol on $ZnMoO_4$ and $MnMoO_4$ catalysts:

The decomposition of isopropyl alcohol on the molybdate catalysts obtained by the solid state reaction has been studied with a view to correlating their physico-chemical characteristics with catalytic activity. The catalysts promote both dehydrogenation and dehydration of isoproply alcohol. This may be ascribed to the almost equal values of apparent energies of activation (E_{app}) for dehydrogenation (9.7 k cal.mole) and dehydration (13.1 k cal.mole). The values of E_{app} for dehydration decreases with increasing MoO_3 content in the case of $ZnMoO_4$, suggesting thereby that MoO_3 is the active component for dehydration reactions.

On $ZnMoO_4$, the dehydrogenation activity is increased in presence of hydrogen but is unaffected by the presence of acetone. On the other hand, on $MnMoO_4$, hydrogen enhances both dehydrogenation and dehydration while acetone suppresses dehydrogenation. The energy gap values obtainted from the electrical conductivity measurements under various atmospheres showed that the hydrogen pretreatment resulted in the increase of the Fermi level. This would suggest that the enhanced dehydrogenation in presence of hydrogen is related to the Fermi level as has been postulated by Wolkenstein [8].

Micro-gravimetric measurements of adsorption of acetone and alcohol in $MnMoO_4$ indicate that the observed suppression of the dehydrogenation of isopropanol on it in presence of acetone, is presumably due to occupation of the dehydrogenation-sites by adsorbed acetone.

The products of decomposition of isopropanol on $MnMoO_4$ included appreciable amounts of propane in addition to the main dehydration product, propylene. The possibilities of propane-formation through hydrogenation of propylene by hydrogen or by self-hydrogenation [9] or by hydrogen-transfer from the alcohol [10] were experimentally examined and eliminated, leaving hydrogenolysis of the alcohol itself as the only plausible mechanism for propane formation, as was found earlier by Balandin [11] for the same reaction on MoO_3.

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1. B. Viswanathan, J. Gopalakrishnan, V. Srinivasan, and M.V.C. Sastri, "Thermal Decomposition of Ferrous and Manganous Oxalates in Vacuum," J. Thermal Analysis, 3, 429 (1971).
2. M. V. C. Sastri, G. Aravamudan, J. Gopalakrishnan, and N. Ramadoss, "Perovskite Type Zirconates from Thermal Decomposition of Tetra Oxalate-zirconates," Presented at the Dept. of Atomic Energy Symposium, Aligarh (Dec. 1972), to be published.

Project Title: INVESTIGATIONS IN THE CHEMICAL AND THERMODYNAMIC PROPERTIES OF REFRACTORY MATERIALS INVOLVING OXIDES, NITRIDES, CARBIDES, ETC., AT HIGH TEMPERATURES

Principal Investigator: Dr. V. V. Dadape

Institution: National Chemical Research Laboratory, Poona, India

NBS Monitor: Dr. W. S. Horton

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

The vaporization of the oxides, nitrides and carbides of aluminum, magnesium, chromium, titanium, zirconium, and other elements were to be studied using the Langmuir, Knudsen, and other techniques; the chemical interactions of these compounds at high temperatures were also to be studied.

The monitor states that at the time this project was initiated and during the period of the grant, the work of transpiration paralleled similar work at NBS. It formed a complement to the Knudsen vaporization of the Inorganic Materials Division.

Results and Implications to Date

The reaction of $A\ell_2O_{3(c)}$ with aluminum monochloride has been investigated at high temperatures (1325, 1380 and 1425 K respectively) by a transpiration technique. The weight loss data obtained at these temperatures and the chemical analysis indicate that the equilibrium reaction:

$$\frac{1}{2} A\ell_2O_{3(c)} + 3A\ell C\ell_{(g)} = A\ell_2O_{(g)} + A\ell C\ell_{3(g)} + \frac{2}{3} A\ell_{(\ell)}$$

holds good and the heat of reaction has been found to be -14.4 ± 1.6 k cal. mole^{-1}.

Solid $A\ell OC\ell$ and its thermal behavior

Crystalline $A\ell OC\ell$ prepared by the reaction of $A\ell_2O_3$ with $A\ell C\ell_3$ in a sealed tube kept at 593 K was found to decompose in the temperature range 723-773 K. The stability of the solid was found to increase in a carrier gas (nitrogen) saturated with $A\ell C\ell_{3(g)}$. The following table indicates the thermal stability of $A\ell OC\ell_{(c)}$ in an $A\ell C\ell_{3(g)}$ atmosphere.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

Temperature in K	Flow rate of nitrogen mℓ./min.	Percent decomposition of $A\ell OC\ell_{(c)}$	Remarks
673	40	20%	No $A\ell C\ell_{3(g)}$ was added to the carrier gas.
723	45	60%	
773	40	Decomposed completely.	
823, 873, 923	35	No decomposition was observed.	Carrier gas was saturated with $A\ell C\ell_{3(g)}$.
973	25	80%	
998	25	95%	
1023	25	Decomposed completely.	

The chemical analysis of the products indicates that the decomposition may be expressed as follows:

$$3A\ell OC\ell_{(c)} = A\ell C\ell_{3(g)} + A\ell_2O_{3(c)}$$

Reaction of $A\ell C\ell_{(g)}$ with $MgO_{(c)}$

The reaction of aluminum monochloride with magnesium oxide was investigated between 1298 and 1465 K employing a flow method. The products of the reaction and the weight loss measurements suggest that the equilibrium reaction was

$$4MgO_{(c)} + 3A\ell C\ell_{(g)} = MgA\ell_2O_{4(c)} + A\ell C\ell_{3(g)} + 3Mg_{(g)}$$

The reaction yielded a third law heat, $\Delta H_{298} = 21.85 \pm 0.84$ k cal. mole^{-1} which compared favorably with the second law value of 24.03 ± 2.49 k cal. mole^{-1}. These values gave -553.36 ± 1.89 and -551.18 ± 3.55 k cal. mole^{-1}, respectively, for the heat of formation of magnesium aluminate from the elements. The heat of formation of $MgA\ell_2O_{4(c)}$ from the oxides at 298 K was found to be 9.26 ± 1.89 k cal. mole^{-1} from the third law and -7.08 ± 3.55 k cal. mole^{-1} from the second law.

Reaction of $A\ell C\ell_{(g)}$ with $BeO_{(c)}$

The results of the studies of the reaction $A\ell C\ell_{(g)}$ with $BeO_{(c)}$ at 1389 - 1492 K suggest the following reaction:

$4\ BeO_{(c)} + A\ell C\ell_{(g)} + A\ell C\ell_{3(g)} = BeO{:}Al_2O_{3(c)} + 2BeC\ell_{(g)} + BeC\ell_{2(g)}$ [$A\ell C\ell_{(g)}$ contained about 10% $A\ell C\ell_{3(g)}$].

Over the temperature range, the ΔH was found to be 103.56 ± 10.29 k cal. $mole^{-1}$. From the recent experimental data and available thermal functions, the $\Delta H_{f_{298}}$ for $BeC\ell_{(g)}$ was found to be + 7.23 ± 5.15 k cal. $mole^{-1}$ by second law and the corresponding third law value was - 5.67 ± 0.60 k cal. $mole^{-1}$.

Vapor pressure of nickel chloride ($NiC\ell_2$)

The vapor pressure of $NiC\ell_2$ was determined over a temperature range 1030 to 1116 K employing a transpiration technique. The vapor pressure equation can be represented as

$$+ \log P_{atm.} = - \frac{11,277.3 \pm 322.65}{T} + 9.0603 \pm 0.3$$

The calculated heat of sublimation is 58.11 ± 1.47 k cal. $mole^{-1}$. The sublimation temperature at 760 mm. pressure was found to be 1244.8 K.

Equilibrium reaction $Ni(c) + NiC\ell_2(g) = 2NiC\ell(g)$

The above reaction was studied between 1278 and 1380 K using a flow method. The $\Delta H_{r_{1329}}$ was found to be 152.66 ± 6.77 k cal. $mole^{-1}$ and the $\Delta S_{r_{1329}}$ = 100.46 ± 5.06 cal. $deg.^{-1}$ $mol.^{-1}$.

Yttrium oxychloride $YOC\ell$

$YOC\ell$ was obtained by heating $YC\ell_3 6H_2O$ at 450-475 K. It loses water and hydrochlorine acid molecules at these temperatures forming $YOC\ell$.

The decomposition study was carried out in an atmosphere of purified argon at temperatures upto 1593 K. The oxychloride was found to decompose as follows:

$$3YOC\ell(s) = Y_2O_3(s) + YC\ell_3(g)$$

After the experiments, the residue in the boat and the gaseous product condensed on a cold finger were chemically and spectrographically analyzed for Y_2O_3 and $YC\ell_3$ respectively. The condensate showed the presence of $YC\ell_3$ only. At 1593 K $YOC\ell$ decomposed completely leaving only Y_2O_3 in the boat.

The results of the dissociation experiments carried out between 1188 K and 1593 K are given in the following table:

Experimental data on the decomposition of $YOC\ell(s)$

Temp. K	$P_{(atms)}$	Log P
1188	9.3884×10^{-4}	-3.0274
1288	1.2257×10^{-3}	-2.9115
1328	1.3730×10^{-3}	-2.8625
1373	1.5368×10^{-3}	-2.8142
1408	1.7713×10^{-3}	-2.7517
1468	1.8479×10^{-3}	-2.7333
1498	2.4417×10^{-3}	-2.6494
1573	3.6090×10^{-3}	-2.4426
1593	3.7039×10^{-3}	-2.4313

Reaction of $NiC\ell_2(g)$ with $Ni(c)$

The equilibrium study of the reaction

$$Ni(c) + NiC\ell_2(g) = 2NiC\ell(g)$$

was carried out between the temperatures 1243 K and 1396 K using the transpiration technique. The heat of reaction $\Delta H_{r_{1320}}$ at the mean temperature was found to be 87.9 ± 4.9 k cal. $mole^{-1}$ and the entropy $\Delta S_{r_{1320}}$ of the reaction was 50.2 ± 3.7 e.u. The entropy of $NiC\ell(g)$ at 1320, calculated from this was 81.1 ± 2 e.u. which compared satisfactorily with that calculated from Brewer's model (77.1 e.u. at 1573 K).

Action of $A\ell C\ell_3(g)$ on $NiO(c)$

The reaction was carried out between 1270 and 1448 K. By a careful consideration of the gaseous products which condensed on the cold finger, the following two reactions are considered:

$$4NiO(c) + 2A\ell C\ell_3(g) = NiA\ell_2O_4(c) + 3NiC\ell_2(g) \qquad ...1$$

$$2NiO(c) + 2A\ell C\ell_3(g) = 2A\ell OC\ell(g) + 2NiC\ell_2(g) \qquad ...2$$

The overall reaction is given by:

$$6NiO(c) + 4A\ell C\ell_3(g) = NiA\ell_2O_4(c) + 5NiC\ell_2(g) + 2A\ell OC\ell(g)$$

The $H_{r_{1359}}$ is 201.2 k cal. mol^{-1} and $S_{r_{1359}}$ is 138.9 e.u.

Study of the reaction between $A\ell F_3(g)$ and $A\ell(\ell)$ by transpiration technique

The reaction $A\ell F_3(g) + 2Al(\ell) \rightleftarrows 3A\ell F(g)$ was carried out in a platinum lined mullite tube between 1295 and 1375 K. The furnace was 24" long and Kanthal wound and had two constant temperature zones.

An E. Merck grade $A\ell F_3$ sample was employed. Its spectrographic analysis showed the presence of Si, Fe, and Cu in traces. The aluminum used was in the wire form (BDH A.R. grade). $A\ell F_3$ and $A\ell$ were kept in platinum and graphite boats respectively.

The aluminum wire was cut into small pieces and purified in a stream of dry, purified argon gas at about 1273 - 1303 K. Thus volatile impurities (if any) were removed. Purified argon gas saturated with $A\ell F_3$ vapor was passed over $A\ell(\ell)$. The amount of aluminum transported during the reaction was known by the loss in weight of the metal contained in the graphite boat.

The third law values for the heat of reaction were obtained from $\Delta H^o_{298} = T(-R\ell nk_p - \Delta Fef)$

where k_p = equilibrium pressure,

Δ Fef values were obtained from JANAF tables,

T is absolute temperature in K.

Experiments were carried out at three temperatures and the corresponding third law values for the heat of reaction are given in the following table:

Temperature in K	ΔH_{298} Third law
1295	52.65 k cal. mole^{-1}
1335	50.06 k cal. mole^{-1}
1375	51.25 k cal. mole^{-1}

W.P. Witt and R.F. Barrow (Trans. Faraday.Soc. 55, 730 1959) have reported a third law value of 57.58 k cal. mole^{-1} for the above reaction.

Reaction of $NiC\ell_2(g)$ with molten aluminum

The reaction between nickel dichloride and molten aluminum was studied at high temperatures by the transpiration method. Gaseous nickel dichloride was passed over molten aluminum between 1298 and 1400 K. An examination of the products remaining in the boat indicated the presence of nickel and aluminum metals. Aluminum trichloride was found condensed in the receiver. In order to study the composition of exit gases, the gaseous products were condensed on a cold finger made of silica. The substance collected on the cold finger was scraped and analyzed chemically and spectrographically revealing the presence of nickel and aluminum. Aluminum metal can be attributed to the dissociation of $A\ell C\ell(g)$. The nickel metal formed by the disproportionation of $NiC\ell(g)$ according to the equations:

$$2NiC\ell(g) = NiC\ell_2(g) + Ni(c) \qquad ...1$$

$$3A\ell C\ell(g) = A\ell C\ell_3(g) + 2A\ell(\ell) \qquad ...2$$

With the above products the following reaction stoichiometry can be written:

$$NiC\ell_2(g) + A\ell(\ell) = NiC\ell(g) + A\ell C\ell(g) \qquad ...3$$

$$2NiC\ell_2(g) + 3A\ell(\ell) = 3A\ell C\ell(g) \underline{\div} NiC\ell(g) + Ni(c) \qquad ...4$$

$$2NiC\ell_2(g) + A\ell(\ell) = A\ell C\ell_3(g) + NiC\ell(g) + Ni(c) \qquad ...5$$

$$2NiC\ell_2(g) + 2A\ell(\ell) = A\ell C\ell_3(g) + A\ell C\ell(g) + 2Ni(c) \qquad ...6$$

$$NiC\ell_2(g) + 3A\ell(\ell) = NiA\ell + 2A\ell C\ell(g) \qquad ...7$$

$$NiC\ell_2(g) + 2A\ell(\ell) = 2A\ell C\ell(g) + Ni(c) \qquad ...8$$

With increase of temperature more and more nickel metal is formed thereby showing that the reaction is endothermic and must occur with an increase in entropy. So reactions 5, 6, 7, and 8 can be neglected.

Out of the reactions 3 and 4, reaction 3 can be neglected on the basis that there is no possibility of the formation of nickel metal. The experimental results obtained, when fitted into the reaction 4, are showing some discrepancies between the values of calculated and observed free energies.

Study of the reaction of $A\ell C\ell_3(g)$ with $Mn_3O_4(c)$

An equilibrium study of the reaction $A\ell C\ell_3(g)$ with $Mn_3O_4(c)$ has been carried out between the temperatures 1213 K - 1433 K, by the transpiration technique using argon as carrier gas. Analysis of the products showed the following stoichiometry:

$$Mn_3O_4(c) + 3.5\ A\ell C\ell_3(g) = 1/2\ A\ell_2O_3(c) + 2.5\ A\ell OC\ell(g) + 3\ MnC\ell_2(g) + C\ell_2(g)$$

Employing the heat content functions, the third law value calculated for the heat of reaction is 210 ± 3.14 k cal. mole^{-1}. From the least square fit for the graph of -log K vs 1/T K a straight line having the slope 199.8 was obtained. This when converted to 298 K using the c_p values yielded a second law value of 214.3 k cal. mole^{-1} for ΔH_r. It can be seen that the two values agree well with one another.

The above values for the heat of reaction gave the heats of formation for $A\ell OC\ell(g)$ $\Delta H_{f_{298}}$ = -89.5 k cal. mole^{-1} and -91.2 k cal. mole^{-1} for second and third laws respectively. They may be considered to be in good agreement with the reported value (-84 ± 5 k cal.mole^{-1}) in view of the complicated nature of the reaction and the temperature dependent errors.

Reaction of $A\ell C\ell_3(g)$ with NiO(c)

Employing the flow technique the equilibrium reaction between $A\ell C\ell_3(g)$ and NiO(c) was studied at temperatures 1269-1440 K. The reaction may be represented as follows:

$$6NiO(c) + 4A\ell C\ell_3(g) = NiA\ell_2O_4(c) + 5NiC\ell_2(g) + 2A\ell OC\ell(g)$$

It yielded a second law heat $\Delta H_{298} = 203.67 \pm 5.04$ k cal. mole^{-1}. A value of -83.59 ± 2.5 k cal.mole^{-1} was obtained for the heat of formation of $A\ell OC\ell(g)$ which is in good agreement with that (-84 ± 5 k cal.mole^{-1})reported in the literature.

Reaction between La_2O_3 and $A\ell C\ell_3$

The thermodynamics of the following reaction:

$$6La_2O_3(c) + 11A\ell C\ell_3(g) = 5LaC\ell_3(c) + 7LaOC\ell(c)\ 11A\ell OC\ell(g)$$

was investigated between 719 and 877 K. $LaOC\ell$ was identified by X-ray analysis of the residue after leaching $LaC\ell_3$ with water. The formation of $A\ell OC\ell(g)$ was noted by the presence of $A\ell_2O_3$ deposit ($A\ell OC\ell$ dissociates into $A\ell C\ell_3$ and $A\ell_2O_3$) on the cold finger. The experimental data was used to calculate the heat of formation of $A\ell OC\ell(g)$ at 298 K and a value for ΔH_{298} - 95.93 k cal. mole^{-1} is obtained. Considering the complicated nature of the reaction this value appears reasonable when compared to the reported value of -84 ± 5 k cal. mole^{-1}.

List of Publications that Resulted from the Project

1. D. Bhogeswara Rao and V. V. Dadape, "Equilibrium Studies of the Reaction $2A\ell(\ell) + A\ell C\ell_3(g) \rightleftarrows 3A\ell C\ell(g)$," J. Phys. Chem. 70, 1349 (1966).
2. D. Bhogeswara Rao and V. V. Dadape, "Reaction of $A\ell C\ell(g)$ with MgO(s)," J. Phys. Chem. 71, 537 (1967).
3. M. Atchayya and V. V. Dadape, "Oxygen Removal Capacities of Light Lanthanon Sesquisulfides and Vaporization of La_2S_3," J. Less Common Metals 13, 559-562 (1967).
4. B. Seshagiri Rao and V. V. Dadape, "Sublimation Pressure of Nickel Dichloride and the Study of the Reaction $Ni(s) + NiC\ell_2(g) \rightleftarrows 2\ NiC\ell(g)$," J. High Temperature Science.

B.1.* MATERIALS SCIENCE AND TECHNOLOGY

Project Title: PLATINUM GROUP METAL COMPLEXES, THEIR PREPARATION, STRUCTURE AND ROLE IN HOMOGENEOUS CATALYSIS

Principal Investigator: Dr. M. M. Taqui Khan

Institution: Indian Institute of Technology, Madras

NBS Monitor: Dr. T. D. Coyle

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

This project is aimed at the preparation of new complexes of ruthenium, osmium, iridium, rhodium, platinum and palladium with tertiary phosphine and arsines, polytertiary phosphines and arsines, alkyl and aryl sulfides, and olefinic and hydrocarbon ligands. It is intended to elucidate their structure and study their catalytic properties in the activation of small molecules like molecular hydrogen, oxygen, and nitrogen. The project is aimed specifically at the homogeneous hydrogenation of alkenes and alkynes catalyzed by platinum group metal complexes.

In regard to the relation to NBS programs, the monitor suggests that the project is of significance since it treats the chemical reactivity of small molecules in the coordination sphere of transition metal ions of catalytic significance. These processes are of interest to NBS in connection with possible approaches to novel reference materials and also from the viewpoint of metal-mediated organic transformations related to water quality problems.

Results and Implications to Date

The platinum metal group ions that have largely been investigated for their catalytic activity in homogeneous hydrogenation include mostly the complexes of rhodium(I), iridium(I), platinum(II), and palladium(II) with a d^8 configuration.(1-4) In the course of the present work, new complexes of ruthenium and osmium with a d^6 or d^5 configuration were prepared, their structures were studied by the usual physicochemical techniques and their catalytic efficiency in the homogeneous hydrogenation of alkenes investigated. The list of complexes prepared is presented in Table I.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

TABLE I

Properties of Ruthenium and Osmium Complexes

	Complex*	Color	Solubility**	Melting Point in °C
1.	$RuC\ell_2(AsPh_3)_3$	brown	very soluble in benzene	210-211°
2.	$RuC\ell_2(diphos)_2$	yellow	soluble in benzene-DMF	295-297°
3.	$RuC\ell(SnC\ell_3)(PPh_3)_2$	brown	soluble in benzene	decomposes on heating
4.	$RuC\ell(SnC\ell_3)(AsPh_3)_2$	yellow	soluble in benzene-DMF	-"-
5.	$RuC\ell(SnC\ell_3)(diphos)_2$	yellow	-"-	-"-
6.	$RuC\ell_2(HgC\ell)(PPh_3)_3$	brown	soluble in benzene and chloroform	-"-
7.	$RuC\ell_2(HgC\ell)(AsPh_3)_3$	brown	-"-	-"-
8.	$RuC\ell_2(AsPh_3)_3(O_2)$	brown	-"-	-"-
9.	$RuC\ell_2(PmePh_2)_2(AsPh_3)(O_2)$	green	-"-	-"-
10.	$RuC\ell_2(PPr^n_2Ph)_2(AsPh_3)(O_2)$	green	-"-	-"-
11.	$RuC\ell_2(PPh_3)_2(AsPh_3)(O_2)$	green	-"-	-"-
12.	$RuHC\ell(AsMePh_2)_3(O_2)$	yellow	-"-	-"-
13.	$RuHC\ell(AsPh_3)_3(O_2)$	brown	-"-	-"-
14.	$RuC\ell_2(HgC\ell)(PMePh_2)_2(O_2)$	brown	-"-	-"-
15.	$RuC\ell_2(SnC\ell_3)(AsPh_3)_3(O_2)$	brown	-"-	-"-
16.	$RuC\ell_2(NO)(O_2)(AsPh_3)_2$	brown	-"-	-"-
17.	$RuC\ell_2(N_2)(O_2)(AsPh_3)_2$	brown	-"-	-"-
18.	$OsC\ell_4(AsPh_3)_2$	pale yellow	soluble in DMSO	218-220°(decomp)
19.	fac-$OsC\ell_3(SbPh_3)_3$	green	-"-	277-280° -"-
20.	$OsC\ell_4(PPh_3)_2$	yellow	-"-	238-240° -"-
21.	$OsC\ell_4(PPr^n_2Ph)_2$	yellow	-"-	225-226° -"-

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* Ph = phenyl
(disphos.) = $[(PPh_2)\ CH_2-]_2$
fac = facial isomer

** DMF = dimethyl formamide
DMSO = dimethyl sulfoxide

TABLE I (Continued)

	Complex*	Color	Solubility**	Melting Point in °C
22.	$OsC\ell_4(PPh_2Me)_2$	yellow	soluble in DMSO	222-224° (decomp)
23.	$OsC\ell_4(SbPh_3)_2$	black	-"-	240-242° -"-
24.	$OsC\ell(SnC\ell_3)(CH_2(PPh_2)_2)_2$	yellow	-"-	decomposes on heating
25.	$OsC\ell(SnC\ell_3)(diphos)_2$	yellow	-"-	-"-
26.	$OsC\ell(HgC\ell)(diphos)_2$	colorless	-"-	-"-

Catalysis of the homogeneous hydrogenation of alkenes by ruthenium (II) complexes of the type $L_3RuC\ell X$ ($L=AsPh_3$, $SbPh_3$, or 2/3 {1,2-bis(diphenylphosphino)ethane} = (diphos), X = $C\ell^-$ or $SnC\ell_3^-$) and $L_3RuC\ell_2(HgC\ell)$ (entries 1-7, Table I) have been studied at 35° and 45°C and one atmosphere of hydrogen. In the case of $L_3RuC\ell X$ complexes, the active catalytic species seem to be hydrides of the general formula, L_3RuHX. Some of these hydrides like $(AsPh_3)_3RuHC\ell$ have been very well characterized.

The catalytic activity of ruthenium(II) complexes is very much dependent on the Π-acceptor character of the neutral ligand L and decreases in the order, $PPh_3 > AsPh_3 > SbPh_3 >$ diphos. The catalytic effect is enhanced when X is a corrdinated $SnC\ell_3^-$ group. Complexes of the type $L_3RuC\ell_2(HgC\ell)$ are non-catalytic in the homogeneous hydrogenation of alkenes.

The enthalpy and entropy of activiation for the hydrogenation of cyclohexene catalyzed by $L_3RuC\ell(SnC\ell_3)$ ($L=PPh_3$, $AsPh_3$) have been found to be 2.1 k cal. mol and -53e.u. ($L=PPh_3$) and 1.3. k cal. mol and -56e.u. ($L=AsPh_3$), respectively. The high value of the entropy of activation supports a polar transition state where molecular hydrogen is split heterolytically into hydride ion and proton by the catalytic ruthenium(II) species. The rate of the hydrogenation reaction is much enhanced in the presence of a basic cosolvent like ethanol, lending further support to the heterolytic fission of molecular hydrogen. The catalysis by ruthenium(II) in the homogeneous hydrogenation of alkenes is different from that by the d^8 ions like iridium(I) and rhodium(I) in the fact that there is no change

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* Ph = phenyl
(disphos.) = $[(PPh_2)\ CH_2-]_2$
fac = facial isomer

** DMF = dimethyl formamide
DMSO = dimethyl sulfoxide

in the oxidation state of ruthenium(II) during the catalytic process.

Ruthenium(II) complexes are also very reactive in the activation of molecular oxygen. The complex $RuC\ell_2(AsPh_3)_3$ combines reversibly with molecular oxygen to form a 1:1 dioxygen complex of the composition $RuC\ell_2(AsPh_3)_3(O_2)$(5) (entry 8, Table I). Complex 8 is paramagnetic, $\mu_{eff} = 2.90$ B.M., corresponding to two unpaired electrons. That the complex reacts with sulfur dioxide to give a sulfato complex is shown by its infrared spectrum. On reaction with molecular hydrogen a hydrido complex of the composition $RuHC\ell(AsPh_3)_3$ is obtained. The displacement reaction of 8 by molecular hydrogen is reversible and the dioxygen complex is reformed on passing molecular oxygen through the hydrido complex in solution. In benzene solution, complex 8 catalyzes the oxidation of triphenylphosphine to phosphine oxide. Though rhodium(I)(6)(7) and platinum(0)(8) catalyze the oxidation of triphenylphosphine, complex 8 is the unique example in ruthenium chemistry that catalyzes such oxidations.

Entries (9-17) in Table I represent other dioxygen complexes of ruthenium(II) prepared as an extension of the program on the activation of molecular oxygen. All the dioxygen complexes mentioned in Table I have been characterized by the infrared peak in the region 850-900 cm^{-1} assigned to O-O stretch of the triangular $Ru\text{-}O_2$ group. Some of the dioxygen complexes have also been characterized by a band in the visible region around 6200 Å,, assigned to a possible $\pi - \sigma$ electronic transition. Detailed calculations are being performed to confirm the above assignment.

Complexes 12 and 13 (Table I), exhibit peaks around 1960 cm^{-1} assigned to the ruthenium-hydride stretching frequency. These complexes are novel because of the presence of peaks characteristic of coordinated dioxygen along with that of hydride. The coordinated dioxygen in compounds 12, 13, and 15 (Table I) is stabilized to reduction to such an extent that it is not reduced in the presence of strongly reducing hydride or $SnC\ell_3^-$ groups. Compound 16 (Table I) contains both coordinated dioxygen and nitric oxide as confirmed by the presence of infrared frequencies characteristic of coordinated dioxygen and nitric oxide. Complex 16 reacts with anhydrous hydrazine in methanol to give complex 17 that has both coordinated dioxygen and dinitrogen. The complex is the first example of a compound that has coordinated dioxygen and dinitrogen and offers great promise as a model for further work on a possible oxidative route for the fixation of nitrogen.

Complexes 18-26 (Table I) represent some of the new osmium complexes that have been synthesized and fully characterized. The work on the preparation of platinum group metal complexes and their use in homogeneous catalysis is being continued with particular emphasis on:

1. Testing the catalytic properties of complexes of osmium, entries 18-26 (Table I) for homogeneous hydrogenation and oxidation.
2. Study of nitrogen fixation by an oxidative route and preparation of complexes similar to that of 17.
3. Study of the catalytic properties of the platinum group metal complexes of polydentate phosphines such as: $PhP(CH_2CH_2P(Ph_2)_2$; $P(CH_2CH_2P(Ph_2)_3$; and $C_2H_4(P(Ph_2)CH_2CH_2P(Ph_2)_2$ as possible bi-functional catalysts in homogeneous hydrogenation.

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1. M. M. Taqui Khan and R. K. Andal, Proc. Dept. of Atomic Energy Symposium (India), 1, 253 (1970).
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3. M. M. Taqui Khan and R. K. Andal, Proc. Dept. of Atomic Energy S

Project Title: ELECTRICAL BEHAVIOR OF PURE AND DOPED OXIDES AND OTHER IONIC SOLIDS

Principal Investigator: Dr. E. C. Subbarao

Institution: Indian Institute of Technology, Kanpur

NBS Monitors: Dr. J. B. Wachtman, Jr.
Dr. H. S. Bennett
Dr. Robert S. Roth

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

ZrO_2 and ThO_2, doped with divalent and trivalent metal oxides, have become interesting as solid electrolytes for fuel and galvanic cells, in oxygen gauges, in magnetohydrodynamic devices, etc. Their use is primarily based on the high oxygen ion conductivity in these materials. The present study aims at relating the defect structure of these doped oxides to the conductivity behavior. The role of size, valence and amounts of the impurity ions will be examined. Electrical conductivity of interest here includes ionic, electronic, and hole conductivity and its variation with temperature, oxygen partial pressure and frequency of measurement. The phase relations in the binary system $ZrO_2 - Y_2O_3$ are clarified, since this system includes materials of interest as refractories, solid electrolytes and in MHD.

The NBS monitor states that from his viewpoint the Indian work is of interest because there is related work at NBS in several areas. First, the work on phase transformations in ZrO_2 and phase equilibria of ZrO_2 complement work by Dr. R. S. Roth on phase equilibria in the ZrO_2-Nb_2O_5 system. Second, measurements of electrical conductivity at high temperatures are of interest to Dr. H.P.R. Frederikse who is studying electrical conductivity in high temperature electrode insulator materials. Third, defect calculations in the fluorite structure parallel similar calculations made at NBS by Dr. A. D. Franklin. The Indian program relates to on-going NBS programs in the sense of providing additional basic data on the general types of behavior under study.

Results and Implications to Date

A. Studies on zirconia

Zirconia has a high melting point (about 2700°C) but its use as a refractory is limited

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

by the two solid state transformations it undergoes at 1170°C from monoclinic to tetragonal and at 2370°C from tetragonal to cubic symmetries. Besides, zirconia - based materials are serious candidates in solid electrolytes, fuel cells and MHD devices. Hence a detailed understanding of the phase transformations and thermal behavior of zirconia is crucial. These studies are summarized in the following four subsections:

(1) Axial Thermal Expansion of ZrO_2 and HfO_2 in the Range Room Temperature to 1400°C.

The materials used were high purity ZrO_2 (total metallic impurity 2000 ppm) from Bhabha Atomic Research Center, Bombay and spectrographic grade (99.9%) HfO_2 from the Wah Chang Corporation, USA. A Tem-Press Research high temperature furnace was used on a General Electric XRD-6 diffractometer to record a number of reflections (ten to twelve) in the range $20^{\circ} < 2_{\theta} < 65^{\circ}$ in air. Filtered CuK radiation and a scanning speed of 0.2 or 0.4° per minute were employed. The position of the recorded peaks were determined with an accuracy of ± 0.02° and the desired temperature was maintained within ± 4°C.

The reflections studied in the case of monoclinic ZrO_2 were $11\bar{1}$, 111, 002, 020, 200, 112, $20\bar{2}$, 022, 220,131 and those in the tetragonal phase were 101, 002, 110, 112, 200, 103, 211, 202. Using the d value equation for the monoclinic lattice and the 200 values, we solved all the possible combinations of the above mentioned reflections by a least squares method to give 170 values for each of the lattice parameters of monoclinic ZrO_2 at each test temperature. The reflections $11\bar{1}$, 111, 002, 020, 200, 021, $21\bar{1}$, 022, 220, 202, 221, 131 for monoclinic HfO_2 were used and 344 values for each parameter were calculated. The lattice parameters at room temperature along with maximum deviations are listed in Table 1.

Table 1

Lattice parameters of ZrO_2 and HfO_2

Phase	Temperature (°C)	a (Å)	b (Å)	c (Å)	(deg)
Monoclinic ZrO_2	Room Temperature	5.1415±5	5.2056±5	5.3128±5	99°18'±5'
Tetragonal ZrO_2	1393	3.6526±15		5.2928±27	
Monoclinic HfO_2	Room Temperature	5.1093±5	5.1686±5	5.2839±5	99°9'±5'
	1400	5.1747±5	5.1897±5	5.3787±5	98°25'±5'

Lattice parameter values, unit cell volumes, cube roots of the volumes and their percentage expansions at various temperatures, in the monoclinic and tetragonal phases of ZrO_2 and for the monoclinic phase of HfO_2 were obtained. The values of the lattice parameters were fitted to an equation of a straight line in order to obtain the axial expansion coefficients. These values are listed in Table 2.

Table 2

Expansion Coefficients of ZrO_2 and HfO_2

Phase	Temperature (range) (^{o}C)	a axis ($x\ 10^6$)	b axis ($x\ 10^6$)	c axis ($x\ 10^6$)	volume ($x\ 10^6$)
Monoclinic ZrO_2	R.T.-1040	10.31	1.35	14.68	26.85
Tetragonal ZrO_2	1400-1150	11.61		16.08	38.37
Monoclinic HfO_2	R.T.-1400	9.34	2.98	13.10	27.18

There are three especially interesting features of the thermal expansion behavior of ZrO_2 and HfO_2.

(i) There is a large extent of anisotropy of thermal expansion shown by the fact that the length of the b_m axis of ZrO_2 and HfO_2 stays essentially constant, am and c_m increase, and B decreases. The anisotropy could be associated with the low symmetry and complex bonding with a considerable amount of covalent character.

(ii) A vibrational anomaly is observed in the thermal expansion behavior of ZrO_2 in the temperature range from 930°C to the transformation temperature. There are indications of a similar pretransformation vibration anomaly in HfO_2 in the range from 1400°C to the transformation temperature.

(iii) In ZrO_2 the length of the b_m axis remains almost constant below 500°C while the real expansion of the b_m axis occurs above this temperature.

(2) Monoclinic-Tetragonal Phase Transition in Zirconia

This investigation was aimed at a study of the mono-clinic-tetragonal transition in ZrO_2 by high temperature x-ray diffraction at a number of test temperatures maintained for sufficient time in the co-existence region. A careful study of the positions and the intensities of the x-ray diffraction maxima in the coexistence region was made to elucidate the mechanism of the transformation during heating and cooling in terms of possible atomic movements and the sequence of changes.

The monoclinic-tetragonal transition in ZrO_2 is spread over the temperature 930-1220°C during heating and 1030-700°C during cooling. Two distinct temperature ranges are identified in the transition regions.

(i) pretransformation region, 930-1100°C and

(ii) co-existence region, 1100-1220°C, in which characteristic reflections of both phases are present in the diffraction pattern.

An anomalous increase in the intensities of $11\bar{1}_m$ and 111_m is observed with increasing temperature in the pretransformation region. The reflections $11\bar{1}$ and 111_m derive their intensities primarily from Zr atoms, while 002_m, 020_m, and 200_m depend mostly on oxygen atoms for their intensities. The anomalous increase in intensities, prominent for $11\bar{1}_m$ and 111_m and slight in case of 002_m, 020_m, and 200_m, is interpreted as a result of Zr atoms coming more and more in phase after changes in their positional parameters because of their vibrational excitation due to special modes. The anomalous expansion in selected d values in this temperature range serves as an additional support for the existence of special vibrational modes in this region.

In the coexistence region it is more appropriate to think of hybrid crystal formation rather than phase separation for the following reasons:

(i) Only one reflection, 101_t, characteristic of the tetragonal form appears at 1110°C, while other lines appear at 1160°C or above. Similarly even after the disappearance of the high index monoclinic lines at about 1190°C, $11\bar{1}_m$ and 111_m persist upto 1220°C.

(ii) With increasing temperature in the coexistence region, many interplanar spacings of the tetragonal form show a contraction instead of the usual thermal expansion to be expected in the case of a distinct phase. Other important characteristics of this hybrid crystal are:

(a) All reflections present in the diffraction pattern can be indexed on either monoclinic or tetragonal structures and neither extra lines, if any, characteristic of this hybrid crystal structure nor any superstructure lines have been observed.

(b) $11\bar{1}_m$, 111_m, and 101_t show interdependence in their temperature dependent intensities in the coexistence region.

Although these observations seem to favor the view of possible hybrid crystal formation as a unique, ill defined structure rather than that through coexisting domains, single crystal data are necessary to shed further light on this problem. The orientation relationship between the two structures is now established as follows:

$$(100)_m \parallel (110)_t$$
$$[010]_m \parallel [001]_t$$

A closer look at the coexistence region in the monoclinic-tetragonal as well as tetraganol-monoclinic transition revealed the validity of the concept of hybrid crystal formation in the coexistence region. It is seen that there exist two distinctly different mechanisms for the transition in ZrO_2 in the two cases of heating and cooling. During heating the Zr atoms are vibrationally excitable and the pretransformation behavior is observed. This gives rise to a considerable spread of the transformation before the transition temperature. On the other hand, during cooling the pretransformation behavior is absent and there is a drastic change in a small temperature range near the transition temperature indicating the instability of the high temperature phase as a whole. This is interpreted as a cooperative change in both short and long range interactions. This distinct difference in mechanisms of the transition, one locally started during heating and the other cooperatively started during cooling, is plausibly suggested to be the origin of the large thermal hysteresis.

(3) Hysteresis and Kinetics of ZrO_2 transformation

Thermal hysteresis and kinetics of the reversible monoclinic-tetragonal transformation in ZrO_2 have been studied by DTA. The experimental variables used were heating and cooling rates, number of heating and cooling cycles, the maximum temperature to which the specimen was heated and the time for which it was held at that temperature. X-ray line broadening studies were also made to estimate the crystallite size of the heat treated specimens. It has been observed that the crystallite size increases quite fast with increasing the maximum temperature to which the specimen was heated during the experiment and also with increasing time of holding at that temperature. The magnitude of the thermal hysteresis for the transformation decreases with increasing crystallite size. However the temperature of the forward transformation is nearly invariant (1170 ± 10°C), while the reverse transformation occurs at 850°C in a specimen having finer crystallites (450 Å) but increases to 1000°C when the crystallite size becomes more than 1200 Å.

DTA technique has also been used to differentiate between the isothermal and athermal kinetics of the transformation. It has been observed that isothermal kinetics are exhibited by specimens having smaller crystallites. However, athermal behavior begins to appear as the crystallite size increases. It has also been found that the annealing of the high temperature tetragonal phase resulted a sudden vertical rise which took place within 2 - 3 seconds in the DTA peak in the cooling direction. ZrO_2 transformation is believed to be martensitic in nature and the phenomenon has been attributed to a burst like phenomenon generally observed in some metallic systems. As expected, the phenomenon was observed only when the tetragonal phase was annealed sufficiently by either increasing the annealing time at a lower temperature or exposing it to a higher temperature so that the transformational strain produced during the forward transition is removed and the martensite nuclei can grow rapidly without encountering any immediate obstacles. At times a number of smaller bursts were also observed. The extent of the major burst depends on the amount of strain remaining in the specimen.

(4) Martensitic Transformation in Zirconia

The material presented above has added important information to the extensive literature available on the phase transformation in zirconia. However, some inconsistencies have been pointed out by Weber. The nature of the transformation was not clear. For example, Murray and Allison explained the observed kinetics in terms of the classical nucleation and growth phenomenon, while Wolten was the first to suggest that the tetragonal-monoclinic phase transformation is martensitic in nature. He based this on the athermal and diffusionless behavior and on the large thermal hysteresis, which he attributed to a shear-type mechanism. A critical evaluation of the experimental data on the monoclinic-tetragonal transformation of ZrO_2 was undertaken. which led to the conclusion that this transformation exhibits many of the characteristics observed in martensitic transitions in metallic systems. This transformation is accomplished by a diffusionless, shear-type mechanism, in which some atoms move by distances less than an interatomic distance while other atoms nearly retain their original positions. An orientation relationship exists between the two phases as follows:

$$(100)_m \parallel (110)_{fct}$$
$$[010]_m \parallel [001]_{fct}$$

The habit planes are reported to be $(106)_m$ and $(010)_m$. The high temperature phase is non-quenchable. Well-crystallized material exhibits athermal kinetics and small crystallites undergo isthermal transformation. The critical crystallite size for athermal behavior is of the order of 10^{-5} cm. In well-annealed samples, the tetragonal-monoclinic transformation takes place with a burst. The forward and reverse transitions have a thermal hysteresis of 150-300°C in the case of ZrO_2. It is possible to obtain the high temperature tetragonal phase at room temperature in a metastable state either by the application of hydrostatic pressure or by the presence of small crystallite sizes obtained by special preparation techniques. Still finer crystallite sizes result in the appearance of metastable cubic ZrO_2 at room temperature. On heating, these metastable phases revert to the stable forms.

The review concludes by identifying areas in which further work is needed.

B. Phase diagram studies on the system ZrO_2 - $YO_{1.5}$

(1) Subsolidus relations in this system at room temperature were determined from studies on samples made by pressing the powders and sintering the pellets at 2000°C. The system consists of three single phase solid solutions - one monoclinic and two cubic, and two two-phase regions at room temperature. The system can be conveniently divided into five regions:

(a) Monoclinic ZrO_2 solid solution: Our results show that a maximum of 3 mole % $YO_{1.5}$ (1.5% Y_2O_3) can dissolve into the monoclinic phase of ZrO_2.

(b) Fluorite-type cubic ZrO_2 solid solution: This is the phase of greatest technological interest. We have found 13 mole % $YO_{1.5}$ (7% Y_2O_3) as the lower limit. The upper limit was found to be 71% $YO_{1.5}$ (55% Y_2O_3). Although lattice parameter measurements were not made for this solid solution, it can be inferred from the shift of the peaks that unit cell dimension increases with $YO_{1.5}$ content, since Y^{3+} ion (0.92 Å) is larger than Zr^{4+} ion (0.79 Å).

(c) Region of coexistence of monoclinic and cubic ZrO_2 solid solutions: The limits of this region are discussed in (a) and (b) above. We have not found the earlier reported two phase region of monoclinic and tetragonal ZrO_2.

(d) Single phase $YO_{1.5}$ solid solution was found from 90 to 100% $YO_{1.5}$ (82 to 100% Y_2O_3). The lattice parameter decreases with increasing ZrO_2 content for these solid solutions.

(e) Coexistence of two cubic solid solutions: Fluorite type cubic ZrO_2 solid solution and cubic $YO_{1.5}$ solid solution coexist between the limits discussed in (b) and (d) above.

(2) DTA studies on the system ZrO_2 - $YO_{1.5}$

ZrO_2 - $YO_{1.5}$ compositions with $YO_{1.5}$ contents of 0 - 8%, which had previously been sintered at 2000°C for 5 hours were subjected to differential thermal analysis with alumina as reference. Using weighed amounts of samples and reported values for the heat effect at the monoclinic tetragonal transformation in pure well sintered zirconia, an estimate of the heat effect at the transformation was made.

(i) At room temperature the monoclinic zirconia solid solution exists from 0 to 3 mole % $YO_{1.5}$. A two phase mixture of monoclinic ZrO_2 solid solution and cubic solid solution exists for compositions containing between 3 and 13% $YO_{1.5}$.

(ii) The monoclinic-tetragonal transformation temperature (1170°C for pure ZrO_2) is reduced with the addition of $YO_{1.5}$ up to a eutectoid composition and temperature. The eutectoid transformation (tetragonal ZrO_2 solid solution - monoclinic ZrO_2 solid solution + cubic ZrO_2 solid solution) is located at about 565°C and about 7.5 mole % $YO_{1.5}$. There is an increase in the magnitude of heat effect at thermoclinic-tetragonal transformation upto 2 mole % $YO_{1.5}$ and then a decrease. The peak of the curve nearly coincides with the limit of solid solubility of $YO_{1.5}$ in monclinic ZrO_2. The magnitude of the heat effect for other compositions is approximately proportional to the amount of the monoclinic phase in the two phase field.

C. The ternary system $ZrO_2 - Y_2O_3 - Nb_2O_5$

Ternary compositions from this system with varying zirconia-yttria ratios at constant niobia contents of 3,5 and 10 % respectively were made by pressing and sintering at 2000°C. The following facts are obtained from the diffraction patterns of these compositions:

(a) On the 3% niobia line cubic fluorite phase extends from 7% yttria to between 45% and 49% yttria.

(b) On the 5% niobia line fluorite phase extends from between 15% and 20% yttria to between 45% and 50% yttria.

(c) On the 10% niobia line fluorite phase extends from between 20% and 25% yttria to between 40% and 45% yttria.

Thus the cubic fluorite type solid solution phase field has a dome-shaped appearance in the ternary system.

In all the above cases a two phase region of monoclinic solid solution and fluorite type s.s. exists on the low yttria content side of the phase diagram. A two phase region of fluorite type s.s. and s.s. of zirconia in yttria appears on the high yttria content side of the phase diagram.

Accurate lattice parameter determinations were done for ternary compositions. The lattice parameters gradually increase with yttria content for any fixed niobia content. This is in accordance with the ionic size consideration for zirconium (0.79 Å) and yttrium (0.92 Å). The lattice parameter for compositions with a fixed zirconia content decreases with increasing niobia content. This is to be expected because the ionic radius of niobium (0.69 Å) is smaller than that of yttrium. The lattice parameter values are consistent with the cubic solid solution field boundaries as established by the disappearing phase method.

The lattice parameter variation with yttria content shows a negative deviation from Vegard's law. But the lattice parameter variation with niobia content show a positive deviation from Vegard's law.

D. Phase diagram and conductivity studies in ThO_2 - CaO system

We took up investigations to study the defect structure and its effect on the electrical properties of ionic solids with the fluorite structure. For this we chose thoria in the pure and CaO doped conditions.

The phase diagram ThO_2-CaO is not well established. The first attempts were to find out the solubility limit of CaO in ThO_2. Samples were made by pressing mixtures of ThO_2 and $CaCO_3$ powders and sintering at 2000°C. The solubility limit was found out both by the disappearing phase method as well as by lattice parameter determinations. The lattice parameter shows a decrease from 0 mole % CaO to 5 mole % CaO. Thereafter it remains constant showing that the solubility limit is between 5 and 10 mole % CaO. This view is supported by the x-ray patterns as one line corresponding to CaO phase appears in the samples containing 10% or more of CaO, while it is absent in samples with less CaO content.

A.C. Electrical conductivity at 1 KHz was measured for samples with 0,1,2,3,4,5,6 and 10 mole % CaO, at 50°C intervals in the temperature range 600 to 1350°C. The conductivity of all the samples can be represented by an Arrhenius type equation:

$$\sigma(T) = A \exp(-E/kT)$$

in major part of the temperature range.

Values of the constant A lie between 0.06×10^5 and 1.24×10^5 and the values of the activation energy E are in the range 1.12 to 1.18 ev. The isothermal conductivities for these samples show an increase with CaO content from 0 to 4 mole % CaO and then remain constant after a slight drop. The activation energies may be taken to be constant within experimental errors. It is observed that the conductivity goes through a maximum at about the composition with 2% of anion sites vacant. This fact is in agreement with the observation on other ThO_2 based solid solutions where a conductivity maximum is observed in compositions with 2 to 3.5% anion sites vacant.

E. X-ray diffraction and conductivity studies on Y_2O_3 solid solutions:

Phase diagram and electrical conductivity studies were done on compositions near the Y_2O_3 end of the ZrO_2 - YrO_2 - Y_2O_3 system. Samples were made by mixing powders of ZrO_2 and Y_2O_3 in the required ratio and sintering them twice at 2000°C with intermediate grinding and pressing.

The solid solubility limit of ZrO_2 in Y_2O_3 was determined by precise determination of lattice parameters and microstructural studies. The lattice parameter decreases with addition of ZrO_2 to Y_2O_3 for 10.603 Å (pure Y_2O_3) to 10.568 Å at 18% ZrO_2 content beyond which it remains constant showing a two phase region. This is confirmed by the microstructure of the single phase and two phase compositions on the two sides of the composition at 18% ZrO_2 in Y_2O_3. A. C. Electrical conductivity at 1 KHz was measured in the temperature range 700°C to 1250°C. The values of log G vs. 1/T can be represented by two straight lines of different slopes in the low and high temperature regions.

The activation energies in the extrinsic region i.e. the low temperature region is about 0.21 ev. while it is about 1.7 ev. in the intrinsic region i.e. the high temperature.

It is suggested that in both the extrinsic and intrinsic regions the defects responsible for electrical conduction are fully ionized yttrium vacancies that generate compensating holes. In the extrinsic region the yttrium vacancies are created by the substitution of Y^{3+} by Zr^{4+} ions. Thus conduction is impurity controlled in the extrinsic region, as evidenced by the increase in conductivity with ZrO_2 content.

In the intrinsic region, the yttrium vacancies responsible for conduction are those created due to existence of a Schottky defect situation in thermal equilibrium. The "Knee" temperature for each composition represents the temperature at which thermally generated yttrium vacancies far out number those due to impurities. The shift of the "Knee" to higher temperatures with increasing ZrO_2 content is in accordance with expectations according to this model.

F. Defect calculations in fluorite lattice

Most solid solutions of high temperature oxides such as ZrO_2, UO_2, ThO_2 etc. have fluorite lattices. Also, the electrical conductivities of such materials are known to be ionic. It was thought, therefore, that detailed defect energy calculations on CaF_2 lattice would help to build up a model for explaining the transport mechanisms involved in these oxides.

Some calculations were carried out on CaF_2 lattice of the activation energies of migration of anion vacancies as well as anion interstitials. The method used was that developed by Franklin. Results showed that the anion vacancy movement occurs along the (100) direction of the lattice. Also, an interstitialcy mode of anion motion is the likely mechanism of transport in lattice having interstitial anions.

The preliminary results have been published.

G. Papers presented at conferences based on work on the project

1. R. N. Patil and E. C. Subbarao, "Studies on the Thermal Expansion Behavior of the Refractory Oxides ZrO_2 and HfO_2 by x-ray Diffractometry," at the 32nd Annual meeting of the Indian Ceramic Society, Madras (July 1968).

2. C. B. Choudhary and E. C. Subbarao, "Cubic Fluoride Type Phase in the Systems ZrO_2 - Y_2O_3 - Nb_2O_5" at the 33rd Annual meeting of the Indian Ceramic Society, New Delhi, (March 1969).

3. R. N. Patil and E. C. Subbarao, "X-ray Diffraction Study of the Monoclinic-Tetragonal Phase Transition in Zirconia," at the VIII International Congress of Crystallography, Stony Brook, New York (August 1969). For abstract, see Acta Cryst.

H. Papers in course of preparation

1. E. C. Subbarao, H. S. Maiti, and K. K. Srivastava,"Martensitic Transformation in Zirconia," (to be published).

2. K. K. Srivastava, R. N. Patil, C. B. Choudhary, K.V.G.K. Gokhale, and E. C. Subbarao, "Revised Phase Diagram for the system ZrO_2-$YO_{1.5}$" (to be published).

I. Theses based on work on the project

1. C. B. Choudhary, "Cubic Fluorite-type Phase in the System ZrO_2 - Y_2O_3 - Nb_2O_5," M. Tech. Thesis, IIT Kanpur (January 1969).

2. C. S. Krishnan, "Some Studies on Y_2O_3 - ZrO_2 System," M. Tech. thesis, IIT Kanpur (January 1969).

3. A. K. Mehrotra, "Electrical Conductivity of the system ThO_2 - CaO," M. Tech. Thesis, IIT Kanpur (January 1971).

List of Publications that Resulted from the Project

1. R. N. Patil and E. C. Subbarao, "Axial Thermal Expansion of ZrO_2 and HfO_2 in the Range Room Temperature to 1400°C," J. Appl. Cryst. 2, 281-288 (1969).

2. R. N. Patil and E. C. Subbarao, "Monoclinic-Tetragonal Phase Transition in Zirconia: Mechanism, Pretransformation and Coexistence," Acta Cryst. A 26, 535-542 (1970).

3. E. C. Subbarao, C. B. Choudhary, A. K. Mehrotra, and R. N. Patil, "Defect Structure and Ionic Conductivity of Zirconia and Thoria," Proc. Symposium on Materials Science Research, Bangalore, Vol. I, 429-435 (February 1970).

4. D. Chakravorty, "Energy of Migration of Anion Vacancy and Interstitial in Calcium Fluorite," J. Phys. Chem. Solids, 32 1091-1092 (1971).

5. C. S. Krishnan and D. Chakravorty, "Electrical Conductivity in Cubic Y_2O_3 - ZrO_2 Solid Solutions," Mat. Res. Bull. 6, 91-96 (1971).

6. H. S. Maiti, K.V.G.K. Gokhale, and E. C. Subbarao, "Kinetics and Burst Phenomenon in ZrO_2 Transformations," J. Am. Ceram. Soc., 55, 317-322 (1972).
7. H. S. Maiti, K.V.G.K. Gokhale, and E. C. Subbarao, "Effect of Heat Treatment on the Kinetics of Zirconia Transformation," Proc. Symposium on Materials Science Research, Hyderabad, 353-363 (February 1972).

B.1.* MATERIALS SCIENCE AND TECHNOLOGY

Project Title: TRANSPORT PROPERTIES OF SOLIDS AT LOW TEMPERATURES

Principal Investigator: Dr. G. S. Verma (Present address: Physics Department
Banaras Hindu University
Varanasi 5 UP, India)

Institution: Physics Department, Allahabad University, Allahabad

NBS Monitor: Dr. A. H. Kahn

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials

Summary Description of Project Goals

The aim was to examine critically and evaluate the role of different phonon scattering processes in thermal transport properties of solids, especially insulators and semiconductors, in the low and high temperature regions.

Results and Implications to Date

A. Thermal transport properties of solids

Simplified expressions for the resonance-scattering relaxation rates for phonons for doped Ge have been obtained for the first time for situations $h\omega_q\lambda >> 4\Delta$, $K_bT >> 4\Delta$ and $h\omega q\lambda << K_bT$ and $K_bT << 4\Delta$, where 4Δ is the energy difference between the donor electron singlet ground state and the first higher energy triplet state [25]**. Hasegawa's angular matrices, which depend upon the geometrical structure of the conduction band, are obtained for Ge. These expressions have been very successfully used in explaining the low temperature phonon conductivity results of Sb-and As-doped and compensated Ge in the off-resonance situations where other phonon scattering processes are also relevant. For doped alkali halides, where the nature of the coupling of the rotational states of the impurities to the phonons is not fully understood, the frequency dependence of the resonance relaxation rates have been established for CN and NO_2 doped alkali halides [18]. Kwok's theory has been modified by including the transitions to the singlet and triplet states from higher energy states which are relevant at higher temperatures. With this modification a partial success has been achieved in explaining the discrepancy between Kwok's theory and the observed temperature dependence of acoustic phonon attenuation in P-doped Ge beyond its maximum [24].

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

** Figures in brackets refer to the List of Publications that Resulted from the Project.

It has been established quantitatively for the first time that for donor electron concentrations greater than $10^{17}/\mathrm{cm}^3$, Ziman scattering of phonons by electrons in the conduction state is responsible for the drastic reduction in the phonon conductivity of Sb-and As-doped Ge. For these heavily doped semiconductors, impurity levels merge with the conduction band. However, in establishing this fact we had to consider the temperature dependence of density-of-state effective mass and the reduced Fermi potential. Fortunately the information regarding the temperature dependence of the reduced Fermi potential was obtained from the thermoelectric data of the same samples. The above conclusions were verified for a large number of Sb-and As-doped Ge samples. The large decrease in the phonon conductivity with the increase in the donor electron concentration is explained in terms of the increase in the deformation potential.

Nowhere in the literature one will find calculations in such a comprehensive scale for the thermoelectric power for η^* (reduced Fermi potential) varying from -22 to +38 and the scattering parameter $S= -\frac{1}{2}, 0, +\frac{1}{2}, +1$ and $+\frac{3}{2}$. The point of these calculations is that if one knows or assumes the nature of the scattering of the electrons by phonons one can read directly the values of the reduced Fermi potential from the graphs for the observed values of the thermoelectric power. Values of F_0, $F_{1/2}$, F_1, $F_{3/2}$, F_2, $F_{5/2}$, F_3 and F_4 for η^* varying from zero to +40 and that of $F_{1/2}$ and $F_{3/2}$ for η^* varying for zero to -24, were not available. These have been calculated for the first time and are available on request.

It was further established that Carruthers' scattering, in which phonons are scattered as a result of virtual transitions of the donor electrons between the ground state and three-fold degenerate first excited state, can explain the drastic reduction in the phonon conductivity of those samples for which the donor electron concentration is less than $10^{17}\ \mathrm{cm}^{-3}$. Values of the shear deformation potential as obtained from the phonon conductivity data are found to lie between 17.8 and 27.9 eV.

It has been shown for the first time that diopolar contributions to thermal resistance due to electrons and holes become important in the lattice thermal conductivity of doped Si-Ge alloys at high temperatures. The phonon conductivity of both n- and p- type Si-Ge alloys with different carrier concentrations has been estimated by calculating separately the contributions of longitudinal phonons and transverse phonons. It has been found that there is good agreement between the calculated temperature dependencies of the total phonon conductivity and the experimentally obtained values of thermal conductivity minus electronic conductivity. The dilatational deformation potential is found to increase with the increase in the carrier concentration and the reduced Fermi potential. The dipolar contribution is found to be significant at temperatures above 700 K for n-type alloys, for which the doping is comparatively low.

In insulators the transport of energy takes place through phonons and heat conduction is adequately described by the interaction between the phonons, impurities, and imperfections. In ferromagnetic insulators at sufficiently low temperatures magnons can also act as the carrier of heat energy. This aspect of phonon conductivity due to magnons has been considered by Sato, Douthett and Friedberg, Harris and Luthi, and Douglass. But all of them neglected magnon-phonon interaction. They considered that magnons and phonons are scattered only by boundaries of grains or of the specimen. Expressions have been derived for magnon-phonon scattering relaxation times for different cases as a function of temperature and wave vector using the theory of Sinha and Upadhya. The appropriate relaxation time is used in the determination of the effective relaxation time for magnons and thermal conductivity of YIG is calculated in the temperature range 0.5 to 70 K considering a quadratic dispersion law for magnons and a Debye spectrum for phonons. Scattering of magnons by defects is also considered. The magnon contribution is shown to be appreciable in the temperature range 0.5 to 2 K. [19].

Values of the nonlinearity constant D, which involves third-order elastic constants, are obtained for silicon from the phonon conductivity data in the presence of point-defect scattering. The results are compared with the theoretical value obtained on the basis of Keating's theory which has been very successful in explaining the third-order elastic constants of Si. It has been shown for the first time that the constant D depends upon temperature and the assumption by the previous workers that it is independent of temperature is not correct. Keating's theory overestimates the value of the non-linearity constant [16]. A similar study for Ge at room and liquid nitrogen temperatures reveals the temperature dependence of D [26]. It is found that Keating's theory fails to explain the third order elastic constants of GaAs as it omits the effect of long range Coloumb forces on harmonic constants [17].

B. Subsidiary work

Solid state acoustics: For the first time the acoustic saturation of individual NMR lines were studied. A generalized expression for the central resonance line corresponding to the ultrasonic transition probability W_{u2}'' is obtained for an arbitrary spin I. This expression, which is same for quadrupolar and pure magnetic relaxations is given by

$$\frac{N_{\frac{1}{2}} - N_{-\frac{1}{2}}}{n_o} = \left[1 + Po + \frac{32W_u{}''_2 T_1}{(2I+1)\,2}\right]^{-1}$$

where $W_u{}''_2 = W_{u\,-\frac{3}{2}\to\frac{1}{2}} = W_{u\frac{1}{2}\to-\frac{3}{2}} = W_{u\frac{3}{2}\to-\frac{1}{2}} = W_{u\,-\frac{1}{2}\to\frac{3}{2}}$, T_1 is the nuclear spin-lattice relaxation time and $P_m - \frac{1}{2}$ is a measure of the radio frequency transition probability $W_{rf\,m\to m-1} = W_{rf\,m-1\to m} = (P_m - \frac{1}{2})\, W\, (I + m)\, (I - m + 1)$. The effect of the acoustic power on the satellites for the different cases is studied in great detail. Some of the affected satellites show interesting behavior in the sense that, instead of the regular saturation behavior, enhancement effect and negative ratios of the population difference to its equilibrium value are obtained for higher values of U, which is a measure of acoustic power [4].

The basic ideas of the jump diffusion model are applied to nuclear spin-lattice relaxation in water and information regarding the influence of temperature on the nature of diffusive motion in water has been obtained. The number of the solid-like vibratory modes initially decreases rapidly as the temperature is increased from 0^oC and at about 40^oC it drops to a value which remains constant up to 92^oC. At room temperature about 40% of the modes are Langevin type and the rest solid like. As many as 50% of the modes of vibration are still solid like near the boiling point. By assuming that the time τ_o during which a molecule stays at a site and performs complicated vibratory motion is the shear relaxation time, values of shear modulus in water at different temperatures and pressures are obtained [3].

A random walk model is applied to dipolar relaxation via atomic diffusion in a bcc lattice containing two nuclear species. Expressions for T_1 and T_2 in the high field and low temperature limit as well as high temperature and low field cases are derived for magnetic field along (100) and (110) directions. For example, for a magnetic field applied along the (100) direction and the high field and the low temperature limit

$$T_1^{-1} = 8.99\, A_I a_o^{-6}\, \nu_I \omega_I^{-2} + A_s a_o^{-6}\, (\nu_I \nu + \nu_s)[0.149\, (\omega_I - \omega_s)^2 + 11.124 \omega_I^{-2} + 12.105\, (\omega_I + \omega_s)^{-2}]$$

$$T_2^{-1} = 8.31\, A_I a_o^{-6}\, \nu_I^{-1} + 0.56 A_s a_o^{-6}\, (\nu_I + \nu_s)^{-1}$$

where

$$A_I = \nu_I^4 h^2{}_I\, (I + 1) f_I,\ A_s = \nu_I^2 \nu_s^2 h^2 s\, (s + 1) f_s$$

Here r, ω, f and ν are the gyromagnetic ratio, resonance frequency, fractional isotopic abundance and jump frequency, respectively. The subscripts I and S refer to the two nuclear species of spin I and S, a_o is the cube edge.

List of Publications that Resulted from the Project

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2. D. P. Tewari and G. S. Verma, "Acoustic Saturation of Nuclear Magnetic Resonance Lines," Nuovo Cimento, 38, 197 (1965).
3. C. M. Bhandari and G. S. Verma, "Thermal Conductivity of Ge-Si Alloys at High Temperatures," Phys. Rev. 138, 4288 (1965).
4. N.K.S. Gaur and G.S. Verma, "Conductivity Effective Mass from Far Infrared Reflection Measurements," Physica 31, 1489 (1965).
5. C. M. Bhandari and G.S. Verma, "Role of Transverse and Longitudinal Phonons in Thermal Conductivity of InSb and GaAs," Phys. Rev. 140, A2101 (1965).
6. N.K.S. Gaur, C. M. Bhandari, and G.S. Verma, "Temperature Dependence of Density-of-States Effective Mass and the Electronic and Phonon Contribution to Thermal Resistance of Doped Si-Ge Alloys at High Temperatures," Phys. Rev. 144, 628 (1966).
7. N.K.S. Gaur, C. M. Bhandari, and G.S. Verma, "Resonance Scattering of Phonons in GaAs," Physica 32, 1948 (1966).
8. N.K.S. Gaur and G.S. Verma, "Temperature Dependence of the Effective Electron Mass in n-InAs," Physica 32, 1110 (1966).
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13. A. Kumar, A.K. Srivastava, and G.S. Verma, "Resonance Scattering of Phonon in KCl:CN," VII Conference on Thermal Conductivity, NBS, Washington, D.C., Nov. 13-16 (1967).

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23. Anil Kumar and G.S. Verma, "Phonon Conductivity of Mg_2Sn," Phys. Rev. 1, 488 (1970).

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25. Anil Kumar, Arun Kumar Srivastava, and G.S. Verma, "Scattering of Phonons by Bound Donor Electrons in Doped Germonium," Phys. Rev., B2, 4903 (1970).

26. R. C. Tripathi and G.S. Verma, "On the Third Order Elastic Constants of Ge at Room and Liquid Nitrogen Temperatures," J. Appl. Phys. 41, 2999 (1970).

27. G. S. Verma, C. M. Bhandari, and Y.P. Joshi, "Longitudinal and Transverse Phonons in the Lattice Thermal Conductivity of GaAs and InSb, 4 Reply," Phys. Rev. B3, 3574 (1971).

B.3.* BUILDING TECHNOLOGY

Project Title: COMPOSITE STRUCTURAL SYSTEMS IN BUILDINGS

Principal Investigator: Dr. J. K. Sridhar Rao

Institution: Indian Institute of Technology, Kanpur

NBS Monitor: Dr. E. O. Pfrang

NBS Institute or Center and Division: Institute for Applied Technology
Center for Building Technology

Summary Description of Project Goals

The following specific topics in "Composite Structural Systems in Buildings" are to be investigated:

1. A comprehensive review of the state of the art of all aspects of structural behavior, fire proofing, elastic and inelastic behavior, shrinkage, temperature and fatigue considerations of structures and structural components.
2. Annotated Bibliography.
3. Experimental and analytical studies on the following types of structures/structural components:
   - (a) Infilled Frames
   - (b) Masonry Walls on Beams
   - (c) Encased Beams in Columns and Infilled Tubes
   - (d) Continuous Beams with Particular Reference to Reinforcement in the Negative Moment Region
4. Mathematical studies would be carried out using discrete analytical models for continuous systems, and also using numerical techniques.

Results and Implications to Date

1. A review of existing literature indicates that while a considerable amount of work has been done all over the world on steel - beam - concrete slab interaction with various types of shear connection, a complete picture of composite action in infilled frames, slabs on steel girds, interaction of frame - slab - wall systems etc., cannot be presented at this time.

   A comprehensive review of the state of the art was thus restricted to steel-concrete beams and a report (300 pages) has been prepared covering (a) Shear

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

connectors, (b) Behavior of composite beams in bending, (c) Elastic analysis and design, (d) Ultimate strength procedures for analysis and design, (e) Limit states and safety factors, (f) Creep, shrinkage and temperature effects, (g) Fatigue and repeated loading effects, (h) Economy of composite beams, and (j) Recommendations for further research. Certain advanced "Computer Studies" on various aspects of interaction are also appended. It is felt that this comprehensive review will be of use to text book writers.

2. An annotated bibliography of nearly 700 references has been prepared. References have been collected up to June 1972.

3. Tests and analytical studies on infilled frames were omitted on the advice of Dr. E. O. Pfrang, Chief, Structures Section, NBS and attention was focussed on walls on beams, encased beams, encased columns, continuous beams and stud shear connectors. The following full scale tests were completed:

(a) Push out tests - 32 specimens
(b) Column tests - 18 "
(c) Encased beams - 7 "
(d) Continuous beams - 6 "
(e) Walls on beams - 17 "

Besides these a large number of control tests on bricks, brick wallettes, mortar, concrete and steel were conducted.

The following reports detailing the experimental findings, computer programs, analytical studies, and theoretical predictions have been completed:

(a) Behavior, analysis, and design of composite columns (Encased steel sections in concrete).

(b) Stength and behavior of shear connectors under static and pulsating loads.

Analysis of experimental data for the following areas have been completed and the final report is awaiting the completion of computer calculations:

(a) Walls as beams
(b) Encased beams
(c) Continuous beams

As a contribution to the area of "Composite Structural Systems in Buildings" the large amount of test data collected can be mentioned. These data throw light on areas not already investigated by previous research workers. The computer programs generated in the course of analytical investigations using IBM 7044 system will be of assistance to other investigators. As an additional outcome from this project can be mentioned the benefit given to ten graduate students of IIT Kanpur, who would not otherwise have undertaken advanced studies.

List of Publications that Resulted from the Project

1. J. K. Sridhar Rao and C. V. S. Kameswara Rao, "Statistical Aspects of Strength and Fracture Behavior of Concrete," in "Proceedings of the International Conference on the Mechanical Behavior of Materials, Kyoto, Japan;"Society for Materials Science, Kyoto, Japan (1972).
2. S. R. Parimi and J. K. Sridhar Rao, "Effectiveness of Random Fibres in Fibre Reinforced Concrete," in "Proceedings of the International Conference on Mechanical Behavior of Materials, Kyoto, Japan," Society for Materials Science, Kyoto, Japan (1972).

B.3.* BUILDING TECHNOLOGY

Project Title: STUDY OF STRUCTURAL ELEMENTS UNDER DYNAMIC LOADING

Principal Investigators: Professor V. Sundararajan and Dr. V. Kadambi

Institution: Indian Institute of Technology, Kanpur

NBS Monitor: Dr. E. O. Pfrang

NBS Institute or Center and Division: Institute for Applied Technology
Center for Building Technology

Summary Description of Project Goals

The research was directed towards an experimental and theoretical investigation of the effects of blast loads on structural elements and structural models. The experimental study was to be concerned with the development of methods of stress and strain measurement in elements under dynamic loading conditions. Theoretical investigations were to be made on the inelastic response of structural systems subjected to blast loads.

Results and Implications to Date

The following investigations have been completed to date:

1. Analysis of transverse impact behavior of simply supported and built-in beams is investigated with and without taking into account the contact deformation. The impact is assumed to be elastic, and Hertz's law of contact deformation is assumed to hold. Experiments have been conducted to verify theoretical predictions. Non-dimensionalized impact force and maximum strain have been plotted against impact parameter which depends on the geometries and the elastic properties of the beam striker.
2. The response of simply supported and clamped beams partially subjected to blast loads has been studied. In the theoretical analysis different types of pressure distribution in shock waves have been considered. Experiments have been conducted using a shock tube as a loading mechanism. The theoretical and experimental results have been plotted in terms of a dynamic amplification factor and a non-dimensionalized dynamic moment against the period ratio.
3. The response of a beam-column to various pulse loads applied symmetrically over a definite span is being investigated analytically. Various types of transverse transient loads are considered. The effect of pulse shape and the duration of the

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

pulse on the response are studied. Numerical results for the responses in terms of the dynamic amplification factor for the deflection and bending moments are presented in a series of non-dimensional curves.

4. The response to blast loading of thin plates with and without cutouts has been investigated experimentally.
5. The elastic and inelastic response to blast loads of structural systems is under continued investigation. The method of analysis is finite-element idealization followed by numerical integration. The method when fully developed will give the response (elastic as well as permanent deformation) of an enclosure (for example a tank) in which an internal explosion occurs. Both rigid-strain hardening and elastic-plastic material behaviors are yet to be studied.

List of Publications that Resulted from the Project

1. V. K. Jadon, V. Sundararajan, and L. S. Srinath, "Analysis of Transverse Impact on Beams," Research report NBS-ME-1, Dept. of Mechanical Engineering, IIT, Kanpur (Aug. 1971).
2. S. K. Banerjee and V. Sundararajan, "Response of Beams to Blast Load," Research report NBS-ME-2, Dept. of Mechanical Engineering, IIT, Kanpur (Nov. 1971).
3. B. Prasad and V. Sundararajan, "Studies on the Blast and Impact Loadings on Beams," Research report NBS-ME-3, Dept. of Mechanical Engineering, IIT, Kanpur, (Dec. 1971).
4. A. Rajamani and V. Sundararajan, "Dynamic Response of Plates to Blast Load," Research report NBS-ME-4, Dept. of Mechanical Engineering, IIT, Kanpur, (Aug. 1972).

Project Title: STUDIES OF THE ELECTRICAL BREAKDOWN AT THE JUNCTION OF METALS AND SOLID DIELECTRICS IN HIGH VACUUM AT HIGH VOLTAGES

Principal Investigator: Dr. H. V. Gopalakrishna

Institution: Indian Institute of Science, Bangalore

NBS Monitor: Mr. F. Ralph Kotter

NBS Institute or Center and Division: Institute for Basic Standards
Electricity Division

Summary Description of Project Goals

This project aimed at providing a better understanding of insulation breakdown at the metal-dielectric junction in vacuum. In particular, the investigation was to cover (a) Reproducibility of breakdown voltages and relation between length of dielectric and breakdown voltage, (b) Relation between dielectric constant and breakdown voltage, (c) The relative importance of anode vs. cathode conditions, (d) Studies with mixed electrodes, different dielectrics with different geometries, and (e) Study of factors contributing to the obtaining of more uniform electric fields or the highest performance for a given set of conditions.

The investigation could both be theoretical and experimental in nature in the high vacuum region with high dc. ac, and impulse voltages.

Results and Implications to Date

The work carried out so far can be summed up under three categories as follows: (1) direct voltage breakdown, (2) breakdown under power frequency voltages, and (3) pre-breakdown phenomena.

(1) Direct Voltage Breakdown

This investigation was conducted on three dielectric materials: polytetrafluoroethylene (PTFE), Polymethyl methacrylate (Perspex), and unglazed electrical porcelain in the form of 13.0 mm rods. The electrodes were of 304 stainless steel 25 mm in diameter and were used in the plane-parallel configuration. Experiments were conducted in vacua ranging from 10^{-4} Torr to better than 10^{-6} Torr.

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

The first phase of the investigation concerned the reproducibility of breakdown voltages over specimens approximately 5 mm thick, and the influence of the methods used for preparing and conditioning the electrodes and specimen to the breakdown voltage. A method of preparing and conditioning was arrived at, which gave the very high breakdown gradients of 14.2 to 16.2 kV/mm for PTFE, 11.0 to 14.8 kV/mm for Perspex and 5.7 to 6.7 kV/mm for porcelain. An inverse relation of the breakdown gradient with the relative permittivity ε_r of the specimen became obvious. After taking into account the field intensification at the junction caused by the presence of the dielectric by a factor β_j, these results have been shown to be in agreement with the constant breakdown gradient criterion proposed by Alpert et al. for plain vacuum gaps. The factor β_j has been called the junction field intensification factor and has a value such that $1 \leqslant \beta_j \leqslant \varepsilon_r$.

The dependence of breakdown voltage on specimen thickness was studied next. An analysis of the results shows that, in general, three ranges of specimen thicknesses exist separated by two transition values ℓ_T and ℓ'_T. Below ℓ_T, the breakdown voltage is limited by the dielectric strength of the specimen. The region between ℓ_T and ℓ'_T is a transition region in which the breakdown may be limited by the dielectric strength or the negative junction phenomenon depending on the negative junction field intensification. Above ℓ'_T, the breakdown is invariably caused by the negative junction phenomenon. For specimen thicknesses greater than ℓ_T, the minimum breakdown voltage has been shown to be given by: $V_b = \dfrac{45.7 \times \ell^{0.6}}{\varepsilon_r}$ kV, where ℓ is in mm. This expression may therefore be used as the criterion for the design of support insulators in vacuum. However, the results show that to support even moderately high voltages, the insulators have to be inordinately long. Therefore, four methods of improving the breakdown voltages were investigated:

(a) Use of epoxy coated cathodes: For all the three dielectrics substantial improvement in breakdown voltage was obtained by using epoxy coated electrodes. This method has two significant advantages in that spark conditioning for electrodes and glow discharge conditioning for the specimen are obviated.

(b) Metallizing the contact area between the specimen and the electrodes: With porcelain, this method resulted in excellent improvement in the breakdown voltage. Metallization was by vacuum deposition of silver. However, with Perspex there was little or no improvement. Strong coatings could not be obtained with PTFE.

(c) Composite dielectric arrangment: The composite arrangement of a porcelain specimen and a thin wafer of PTFE at the cathode end gave breakdown voltages corresponding to a single PTFE specimen of combined length. This method is useful in improving the breakdown voltage over high permittivity support insulators.

(d) Cascaded insulator assembly: From the equation given above, the breakdown voltage is found to be nonlinearly dependent upon specimen thickness. Therefore, if a given vacuum gap is subdivided by metallic spacers and each subgap supported by insulators, the breakdown voltage would be the sum of the breakdown voltage of the individual gaps. This would then be more than the breakdown voltage of a single insulator of the same total length. Experiments with two and three subgap assemblies were conducted and the results indicate the necessity for voltage grading when the number of subgaps is more than two.

(2) Breakdown Under Power Frequency Voltages

In order to compare the results obtained with direct voltages, experiments with alternating voltages at power frequency were conducted with the same type of electrodes and dielectric specimens under similar conditions. The breakdown gradient for PTFE specimens decreased from about 15 kV/mm for a 2 mm thick specimen to 7.5 kV/mm for a 10 mm thick specimen. For Perspex, it decreased from 11 kV/mm (2 mm thick) to 6 kV/mm (15 mm thick) and for porcelain 7 kV/mm (2 mm thick) to 4 kB/mm (20 mm thick). A comparison of the breakdown performance of the solid dielectrics between ac and dc revealed the following: (i) The breakdown voltage with ac for a given dielectric is generally lower than that obtained with dc, (ii) The luminous glow on the surface of the dielectrics, known as surface charging, is pronounced with ac, and (iii) Metallization of the surface of the specimens in contact with the electrode surface has an adverse effect on the breakdown voltage with ac. It should be noted that this has a definite beneficial effect with dc in improving the breakdown voltage.

Thus the experimental results showed an inferior performance of the dielectric materials with alternating voltage. A straightforward application of the constant breakdown gradient theory of Alpert et al. for plain gaps with direct voltage, does not seem to explain in full the breakdown phenomena with alternating voltages. It was felt necessary that a study of prebreakdown phenomena of clean gaps with ac may throw some light on the behavior of the breakdown across solid dielectrics.

(3) Prebreakdown Phenomenon

With alternating voltages, the gap current consists of (i) a displacement current, due to the gap capacitance, in quadrature with the applied voltage and (ii) a current, in phase with the voltage, with a highly distorted waveform and varying nonlinearly with the voltage. Measurements of the peak values of the latter current were done at various voltages for different gap spacings of 1 to 6 mm by the use of oscilloscopes. Similar measurements were also conducted with dc. The important results are: (i) The in-phase component of the current with ac was due to field emission, (ii) The emission current with ac, for given gap spacing and voltage, was two or three orders more than that with direct voltage, and (iii) The Fowler-Nordheim [1][1] plot (F-N plot) with ac showed a bend towards a higher field intensification factor whereas the F-N plot with dc was a straight line. This shows that the emission current with ac cannot simply be explained by the Fowler-Nordheim theory alone. The effect of space charge, desorption of gases and lowering of work function of the electrode material may be responsible for the bend. (iv) The value of field intensification factor was two or three times more than that with the direct voltage for any gap spacing.

An examination of the electrode surface after multiple breakdowns with ac and dc gave some interesting results. The patchy areas on the anode surface contained a large number of shallow craters with smooth, round rims. The

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[1] Figures in square brackets indicate the publication reference at the end of this project review.

> cathode, on the other hand, had craters which appeared to be deeper with irregular lips with tear-like globules, possibly due to melting of metal. Thus the damage on the cathode was distinctly different from that of anode. With ac, both electrodes had identical damage, similar to that of the anode in the dc case. This could mean that in clean gap the breakdown mechanism with ac is the mechanism responsible for the anode damage with dc.
>
> It is seen that the prebreakdown phenomena in clean gap with ac has some significant differences compared with dc. In particular the increased emission current and increased value of the field itensification factor seem to have a direct bearing on lowering the breakdown voltage across solid dielectrics in vacuum with ac.

The NBS monitor states that from his viewpoint the Indian work represents a significant contribution toward meeting the need felt by the High Voltage Measurements Section staff for an improved understanding of the phenomena associated with electrical breakdown in their efforts to design more compact and reliable facilities for high voltage measurements research and to respond more effectively as consultants to others involved in the design of equipment requiring high voltage insulation.

References:

1. R. H. Fowler and L. W. Nordheim, "Fowler-Nordheim Plot," Proc. Roy. Soc., A 119, 173 (1928).

List of Publications that Resulted from the Project

1. G. R. Nagabhushana, G. Parthasarathy, and H. V. Gopalakrishna, "A Generalized Theory of Direct Voltage Breakdown Across Solid Dielectrics in Vacuum," Proceedings of the IVth International Symposium on Discharges and Electrical Insulation in Vacuum, Waterloo (1970).
2. G. Parthasarathy and H. V. Gopalakrishna, "Prebreakdown Phenomenon in Vacuum Gaps Subject to Alternating Voltages," Proceedings of the IVth International Symposium on Discharges and Electrical Insulation in Vacuum, Waterloo, 214 (1970).
3. G. R. Nagabhushana, G. Parthasarathy, and H. V. Gopalakrishna, "Director Voltage Breakdown Across Solid Dielectrics in Vacuum: Effects of Conditioning of Specimen and Electrodes," 2nd Conference on High Voltage Insulation in Vacuum, Institution

of Electrical Engineering, London, 68 (1971).

4. G. Parthasarathy and H. V. Gopalakrishna, "Breakdown Over Solid Dielectrics in High Vacuum at Power Frequency Voltages," Proceedings of the Vth International Symposium on Discharges and Electrical Insulation in Vacuum, Poland, 321 (1972).

5. G. R. Nagabhushana and H. V. Gopalakrishna, "Methods of Improving the Breakdown Voltage Over Solid Dielectrics in Vacuum," Proceedings of the Vth International Symposium on Discharges and Electrical Insulation in Vacuum, Poland, 339 (1972).

B.11.* NUCLEAR AND RADIATION TECHNOLOGY

Project Title: EXPERIMENTAL INVESTIGATIONS ON THE GENERALIZED OPTICAL MODEL PARAMETERS OF FAST NEUTRONS

Principal Investigator: Professor A. M. Ghose

Institution: Bose Institute, Calcutta

NBS Monitor: Dr. Robert B. Schwartz

NBS Institute or Center and Division: Institute for Basic Standards
Nuclear Radiation Division

Summary Description of Project Goals

The nucleus is a very complicated many-body system of particles and at the present state of our knowledge, there is no easy way following which the basic properties of nuclei can be derived logically from the known interaction processes between any two nucleons. We are, therefore, forced to develop semi-empirical models which are valid for certain regions of energy. The optical model is one of the most successful models of nuclear reactions for moderate energy neutrons interacting with nuclei which are not too light. Apart from its theoretical utility, the model is extremely useful in the design of radiation shielding for fast particles and other fields of practical importance. The object of the present project is to measure fast neutron nuclear reaction and scattering cross sections accurately, so that the values of the empirical parameters occurring in the optical model can be determined precisely. The polarization measurements will directly yield the values of the spin-orbit interactions, which are not sensitive at all to other methds of investigations.

The experimental program will consist of measurements of the total elastic and non-elastic cross sections, and differential elastic cross sections, for the interaction of fast neutrons with nuclei. In addition, polarization during elastic scattering, and the cross sections for formation of some excited states may be measured. These data will be used to determine optical model parameters, and to study their variation with mass number and energy.

Results and Implications to Date

(1) Measurement of nonelastic cross sections

Nonelastic cross section of neutrons at 14.2 and 14.8 MeV have been measured for several nuclei of low, medium, and high atomic number elements. The modified sphere

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

transmission technique developed in this Laboratory has been employed for the measurement of the nonelastic cross sections. The transmission data have been corrected for multiple scattering and for energy loss by elastic collision. The first correction has been obtained by using the polynomial extrapolation method, a detailed theoretical justification for which has already been given by us [1][1]. The second correction has been obtained by the two-bias method developed in this Laboratory [2]. In effect, we have developed a neutron counting method in which all elastic neutrons are detected with equal efficiency while the inelastic ones are completely cut off.

The measured nonelastic cross sections have been compared with the cross section values calculated on the basis of existing local and nonlocal optical model calculations. The present experimental data cannot be fitted to either of the two sets of calculated values. This comparison enforces the justification for a reevaluation of the optical model parameters. To make this calculation successful we need very many cross section measurements for different nuclei and different neutron energies. For this purpose a plan is being worked out with the Department of Atomic Energy, Government of India, to carry out measurements at different energies using accelerators available at Trombay.

(2) Measurement of Absolute (n,2n) cross sections

Absolute (n,2n) reaction cross sections of several nuclei have been measured at three different neutron energies - 14.2, 14.5, and 14.8 MeV. The absolute neutron flux has been measured within ± 3 percent by using a heavily biased plastic scintillation detector and using the theory of the response of organic scintillators to fast neutrons as developed by us [3]. The absolute activity of the irradiated samples has been measured using a coincidence spectrometer. The spectrometer was calibrated within ± 2 % by using a standard ^{22}Na source obtained from NBS. The measured cross sections have error limits ranging from 5 to 10 %.

The literature cross section values show some large difference in the measured values. This is probably due to the inaccuracies in the measurement of the activity of the irradiated samples. We have tried to minimize this by taking into account one

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[1] Figures in square brackets indicate the publication reference at the end of this project review.

important source of error which is often overlooked in this field, namely, the error arising from the finite dimensions of the irradiated targets. We have also observed that measured cross section values when plotted against the asymmetry parameter show no shell structure effect.

The NBS monitor states that from his viewpoint the Indian work will provide important data for a proposed neutron dosimetry standards program within NBS. Both the cross sections which are explicitly measured under this project, and the improved optical model calculations which may result from these data may contribute significantly to the program of NBS.

References:

1. A. M. Ghose, Nucl. Instr. and Methods 35, 45 (1965).
2. A. Chatterjee and A. M. Ghose, Phys. Rev. 161, 1181 (1967).
3. A. Chatterjee and A. M. Ghose, Trans. Bose Institute, 29, 2 (1966).

List of Publications that Resulted from the Project

This is a new project and so far only one paper has been presented:

B. Pal, A. Chatterjee, and A. M. Ghose, Proc. Nucl. Phys. & Solid State Physics Symp. 14B, 33 (1972).

Project Title: INVESTIGATIONS ON THE INTERACTION OF GAMMA RAYS WITH MATTER

Principal Investigator: Dr. A. M. Ghose

Institution: Bose Institute, Calcutta

NBS Monitors: Dr. E. G. Fuller (1966-1969)
Mr. J. H. Hubbell (1970 on)

NBS Institute or Center and Division: Institute for Basic Standards
Center for Radiation Research

Summary Description of Project Goals

The aim of the project was to investigate some of the fundamental interactions of gamma rays with matter. The specific areas which were proposed to be investigated included the measurement of photoelectric cross-sections, coherent and non-coherent scattering phenomena, pair production phenomena etc. Development of new experimental techniques and specialized instruments formed an integral part of these investigations. The results obtained were proposed to be utilized for a better understanding of interaction processes of radiation with matter and for probing the electronic structure of the heavier atoms.

Results and Implications to Date

A scintillation counter was developed which had constant efficiency over the photon range .25 to 1.5 MeV. This counter consisted of a Tl doped NaI crystal with a perforated Al filter.

A scintillation detector was developed which divided the light output from a single NaI(Tl) crystal between two photomultipliers (by means of a perforated reflecting Al foil mounted at 45°) and then took coincidence counts.

Using the sphere transmission method described in the first paper arising from this project, the investigator measured the atomic photoeffect cross section for 1.17 and 1.33 MeV gamma rays (from Co^{60}) in Hg and Pb. In Pb the cross section was also measured using .662 MeV (Cs^{137}) and .835 MeV (Mn^{54}) gamma rays.

The coherent scattering cross sections for .145 MeV gamma rays (Ce^{141}) by atoms of C, Al, Fe, Cu, Sn, and Pb were measured over the angular range 2.67° to 25.40°. The coherent scattering cross section of 1.33 MeV (Co^{60}) gamma rays by Pb were measured over the range 10° to 25°. These results were compared to form-factor calculations based on the

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

Thomas-Fermi and Hartree-Fock approximations. Agreement was better when the Hartree-Fock approximation was used.

Coherent scattering cross sections of gamma rays are best known in the non-relativistic region. In the relativistic region, the values of this important parameter have been calculated, with great difficulty, for only a few isolated cases. To overcome this difficulty an empirical formula was developed for estimating coherent scattering cross sections of X-rays of energies below 1.5 MeV and in the range of 0- 2.5 mc units of momentum transfer. The formula was compared with the experimental data available in the literature for Pb, Sn, and Cu scatterers for different photon energies between 0.279 and 1.33 MeV. Experimental data, in general, were found to be in good agreement with the results of the empirical formula, the deviation being within ± 10% in most cases. The empirical formula was also compared with the form factor results of Nelms and Oppenheim [1][1] and with the predictions of Brown and Mayers [2]. The latter were in excellent agreement with the empirical formula.

The empirical formula obtained was of the form:

$$\sigma\ (\Theta) = \frac{1}{2}\ (1 + \mathrm{Cos}^2\Theta)\ \phi(E,q)\ \left(\frac{Z}{82}\right)^{n(q)}\ f_r(q)$$

where $\phi(E,q)$, $n(q)$, and $f_r(q)$ were relatively simple algebraic expressions for the parameters involved.

Although approximate theoretical estimates of electronic charge distribution in atoms have been reported in the literature, to our knowledge, no study of these distributions based mainly on experimental results has yet been reported for heavy elements. In fact above Z = 10, X-ray techniques cannot resolve K and L shells. We therefore undertook the present work with a view to determine the electronic charge distribution for heavy elements using the experimentally measured coherent scattering cross section data. The present method for determining the value of electronic charge distribution involves the determination of the atomic form factor F(q,Z) for a wide range of momentum transfer q from the experimental values of coherent cross sections and to carry out the numerical integration over q using the usual formula

$$P(r) = \frac{1}{2\pi^2 r\ h^2} \int_0^\infty .F(Z,q)\ \mathrm{Sin}\ \frac{Qr}{h}\ q.dq$$

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[1] Figures in square brackets indicate the publication reference at the end of this project review.

where P(r) is the electronic charge density at a distance r from the center of the atom.

We have calculated the electronic charge distribution for lead. The comparison of the result thus obtained with the Hartree-Fock self-consistent field model shows reasonably good agreement except close to the nucleus. Therefore we may conclude that the present method for determining the electronic charge density distribution is feasible although to compare theoretical and experimental distributions more accurate experimental measurements on the coherent scattering cross sections for high momentum transfers are essential.

In addition to closely related experimental programs at NBS such as the K-shell Compton scattering measurements of Dr. J. W. Motz, NBS is a critical consumer of such data in its program of radiation transport calculations by M.J. Berger and others in the Radiation Theory Section. Also, NBS has since 1952 continued a program of collection, evaluation, and compilation of data on gamma-ray interactions with matter, and at present the OSRD supports this activity within the Radiation Theory Section in the form of an "X-ray Attenuation Coefficient Information Center" under the present direction of Mr. J.H.Hubbell.

The monitor states that from his viewpoint the Indian work is a useful adjunct to gamma-ray interaction studies carried out in the US and elsewhere. In the context of the NBS x-ray data compilation project, the Bose Institute experimental results have in some cases filled gaps in the available data, and in others have provided useful independent data to combine with measurements taken elsewhere. However, the value of some of the associated theoretical analysis, such as the empirical formulas for coherent scattering and K-shell photoeffect may be somewhat short-lived as a result of extensive new all-Z calculations of coherent and incoherent scattering functions (0.1.95 mc units of momentum transfer) by D. Cromer (Los Alamos) and photoeffect (1 keV-1 MeV, total and all subshells including K-shell) by J. Scofield (Livermore).

References:

1. A. J. Nelms and I. Oppenheim, J. Res. NBS, 55, 53 (1955).
2. G. E. Brown and D. F. Mayers, Proc. Roy. Soc., London, A242, 89 (1957).

List of Publications that Resulted from the Project

1. A. M. Ghose, Nucl. Instr. and Meth., 35, 45-54 (1965).*
2. A. Nath, Tras. Bose Res. Inst., 29, No. 2, 51-83 (1966).

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* Although publication of this paper procedes the final signing of the grant, the work was carried out in anticipation of its activation.

3. A. Nath and A. M. Ghose, Nucl. Phys. & Solid State Phys., (India), 260-264 (1966).

4. A. M. Ghose, Nucl. Phys. & Solid State Phys., (India), 10A, 85 (1968).

5. A. Nath and A. M. Ghose, Nucl. Phys. & Solid State Phys. (India), 9A, 519 (1967).

6. A. Nath and A. M. Ghose, NBS Technical Note 442 (1968).

7. S. C. Roy, A. Chatterjee, and A. M. Ghose, Nucl. Phys. & Solid State Phys. (India), 11B, 193-197 (1968).

8. S. C. Roy, A. Chatterjee, and A. M. Ghose, Nucl. Instr. & Methods 67, 318-322 (1969).

9. S. C. Roy and A. M. Ghose, Nucl. Phys. & Solid State Phys.,(India), 12B 65-69 (1969).

10. A. Nath, Nucl. Phys. & Solid State Phys., (India), 12B, 76-80 (1969).

11. M. Biswas, S. C. Roy, and A. M. Ghose, Nucl. Phys. & Solid State Phys., (India), s 13B, 183-186 (1970).

12. S. C. Roy and A. M. Ghose, Nucl. Phys. & Solid State Phys., (India), 13C, 121-124 (1970).

13. M. Biswas, S. C. Roy, and A. M. Ghose, Nucl. Phys. & Solid State Phys., (India), 13B, 483-486 (1970).

14. S. C. Roy and A. M. Ghose, Nucl. Phys. & Solid State Phys., (India), 14C, 79 (1971).

B.11.* NUCLEAR AND RADIATION TECHNOLOGY

Project Title: GAMMA RAY SCATTERING, PART I.

Principal Investigator: Professor P. P. Kane

Institution: Indian Institute of Technology, Bombay

NBS Monitor: Dr. J. W. Motz

NBS Institute or Center and Division: Institute for Basic Standards
Applied Radiation Division

Summary Description of Project Goals

The elastic scattering of 1.12 MeV and 1.33 MeV gamma rays by electrons bound to eight different types of atoms (ranging in atomic number from copper to lead) was to be studied. Differential cross sections for scattering angles between 90° and 124.5° were to be measured.

The Compton scattering of 1.12 MeV gamma rays from electrons bound to heavy elements was to be studied for a number of different scattering angles.

Results and Implications to Date

The elastic scattering differential cross-sections mentioned were measured and reported in the various papers mentioned at the end of this report. The results may indicate a dispersive Delbrück scattering amplitude at 124.5°; further investigations on this point are to be carried out under a subsequent contract.

The Compton scattering measurements were made at 60°, 90°, and 120°; some measurements were also made at 25°.

A byproduct of this work was a review article, entitled "Possibilities of Observation of Nonlinear Quantum Electrodynamic Effects in Vacuum," published in Reviews of Modern Physics.

List of Publications that Resulted from the Project

1. P. P. Kane and G. Basavaraju, "Elastic Scattering of 1.33 MeV Gamma Rays at High Momentum Transfer as a Function of Atomic Number," Proc. Nuclear and Solid State Physics Symposium, Kanpur, 9A, 507-512 (1967). (Dept. of Atomic Energy, Government of India, Publishers).
2. P.P. Kane, "Real Part of the Delbruck Scattering Amplitude and its Experimental

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[*] The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

Verification at 124.5°," ibid, 513 (1967).

3. P. P. Kane and G. Basavaraju, "Possibilities of Observation of Non-linear Quantum Electrodynamic Effects in Vacuum," Rev. Mod. Phys., 39, 52-58 (1967).
4. P. P. Kane, Paper "Recent Work and Immediate Prospects in X-Ray and Gamma Scattering," Proc. Nuclear and Solid State Physics Symposium, Bombay, 11A, 87-105 (1968). (Dept. of Atomic Energy, Government of India, publishers).
5. P. P. Kane and P. N. Baba Prasad, "Compton Scattering by K-shell Electrons at 1.12 MeV-I," Proc. Nuclear and Solid State Physics Symposium, Roorkee, 12B, 81-83 (1969). (Dept. of Atomic Energy, Government of India, publishers).
6. P. P. Kane and P. N. Baba Prasad, "Compton Scattering by K-shell Electrons at 1.12 KeV-II," Proc. Nuclear and Solid State Physics, Madurai, 13B, 187-191 (1970). (Dept. of Atomic Energy, Government of India, publishers).

B.11.* NUCLEAR AND RADIATION TECHNOLOGY

Project Title: GAMMA RAY SCATTERING, PART II.

Principal Investigator: Professor P. P. Kane

Institution: Indian Institute of Technology, Bombay

NBS Monitor: Mr. John H. Hubbell

NBS Institute or Center and Division: Institute for Basic Standards
Center for Radiation Research

Summary Description of Project Goals

The objective was to carry out a study of elastic and Compton scattering of 1.12 MeV and 1.33 MeV gamma rays by atomic electrons.

Results and Implications to Date

The desired measurements were made, using sodium iodide counters. The results were compared to theoretical predictions and the apparent implications regarding the real Delbrück scattering term were given in some detail in the 1970 Nuclear Physics paper.

Studies done up to now were carried out using a sodium iodide counter with a resolution of only six to seven percent at the experimental energies. It is intended to acquire a lithium drifted germanium counter with a resolution of about three tenths of one percent, and to carry our further experiments varying the photon energy, angular range, and target materials; the choice of ranges and materials will be made in the light of the results obtained. The results will be compared with theoretical predictions as before.

List of Publications that Resulted from the Project

1. P. P. Kane and G. Basavaraju, "Elastic Scattering of 1.12 MeV and 1.33 MeV Gamma Rays Through 90° and 124.5° by Different Elements and the Real Parts of the Delbruck Scattering Amplitudes," Nuclear Phys. A149, 49-62 (1970).

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* The alphanumeric designation refers to the NBS Program Structure (see Appendix II).

APPENDIX I

SFCP (PL 480) BACKGROUND HISTORY

Since the Fiscal Year (FY) 1961 the National Bureau of Standards has had an active Special Foreign Currency Program (SFCP) in India, Israel, and Pakistan. During 1970, Yugoslavia was added to the list of countries and Poland and the Arab Republic of Egypt in 1972.

The relevant US laws, such as PL-480 of the 83rd Congress pertaining to the use of SFCP funds, callenge imaginative implementation at the same time as they offer the opportunity for international collaboration to universal benefit. In the mission area of NBS and with the available countries, Dr. Lewis M. Branscomb, former Director of NBS, had called for an effective program. To this end, Mr. H. Steffen Peiser, as program manager, under the supervision of Dr. E. L. Brady, Associate Director for Information Programs, has received wide-ranging support, which is hereby gratefully acknowledged.

Stated Policy for NBS/SFCP Grants

NBS/SFCP grants provide supplementary resources that provide an appropriate means for accomplishing NBS objectives, consistent with U.S. foreign policy objectives. NBS criteria for this purpose are:

"1. All projects must be of scientific or technological excellence.

2. All projects must be within the mainstream of NBS interests or contribute directly to NBS effectiveness.

3. All projects must benefit both the U.S. and the participating countries:

    (a) NBS/SFCP funds must not merely replace otherwise available country funds; and

    (b) Individuals or institutions abroad must not become primarily dependent upon NBS for long term support.

4. All projects must be followed closely by NBS staff members working in related areas. Thus, one or more NBS staff should maintain a continuing direct relationship with the foreign person or group. This relationship should be strengthened by visits in either or both directions.

5. NBS involvement with a technical institution of another nation should be consistent with U.S. foreign policy. For example, relationships with sister institutions, staff exchanges, and visits should be carried on in the context of overall U.S. objectives in its relationship with the other country.
6. NBS staff travel to participating foreign countries should be exploited, when practical, by suitable additional itinerary to identify additional targets for bilateral benefit or to provide additional strength to existing relationships. Such travel should be coordinated with the NBS/SFCP Manager."

Bureau Level Management

Mr. H. Steffen Peiser has been designated the NBS/SFCP Manager by the Director. As such he has the following responsibilities and authorities:

"1. Makes final decisions on grant proposals, allocates funds, and signs SFCP documents.

2. Serves as the principal point of contact with:

    a. The Director on NBS/SFCP policy,
    b. The Institutes and Centers on specific proposals and program planning,
    c. The Budget Division on all budget related matters,
    d. The Procurement Section on grant execution and administrative matters,
    e. The Office of International Relations on matters of channelling communications and relations with the Department of State.

3. Authorizes all foreign travel related to the activated or potential NBS/SFCP grants."

Institute Level Management

Each major organizational unit has the following responsibilities:

"1. Technically evaluates proposals and determines whether the proposals meet Criteria 1, 2 and 4 of the SFCP policy statement for support under the program.

2. Recommends proposals to the SFCP Manager for support and makes priorities known to him.

3. Assures that there is continuing involvement by the designated monitor once a grant has been let.

4. Advises and assists the SFCP Manager in formulating program plans and budget requests."

APPENDIX II

NBS PROGRAM STRUCTURE

A. Promoting Accurate, Meaningful and Compatible Scientific and Technical Measurements

1. Physical Measurement Methods, Units and Standards
2. Measurement Transfer Services
3. Time and Frequency Dissemination Services
4. (Not used)
5. Standard Reference Data
6. Standard Reference Materials
7. (Not used)
8. Materials Measurement Methods and Standards
9. Properties of Matter
10. Exploratory Research

B. Promoting More Effective Use of Science and Technology

1. Materials Science and Technology
   a. Metallurgical Materials
   b. Polymeric Materials
   c. Inorganic Materials
   d. Composite Materials
   e. Dental Materials
   f. Chemical Materials
2. Environmental Pollution Measurement Methods and Standards
   a. Air
   b. Water
   c. (Not used)
   d. Noise
   e. Electromagnetic
3. Building Technology
4. Computer Science and Technology
5. Analysis of Technical Systems
6. Electronic Technology
7. Cryogenic Technology
8. Technology Utilization Analysis
9. Failure Avoidance
10. (Not used)

11. Nuclear and Radiation Technology

12. Illumination Technology

C. Promoting Strength in the Economy and Equity for Buyer and Seller in Trade

1. Voluntary Engineering Standards

2. Measures of Quantities Important to Commerce

3. Product Performance

4. Testing Laboratory Evaluation

5. Fair Packaging and Labeling

D. Standards and Test Methods for Protection of the Public from Specified Hazards

1. Fire Research

   a. Flammable Fabrics
   b. Fire Research and Safety

2. Radiation Safety

   a. Radioactivity
   b. X-rays and Other Ionizing Radiation
   c. Microwave Radiation
   d. Laser Radiation
   e. Ultrasonic Radiation

3. Product Safety

LIST OF SFCP GRANTS IN INDIA

Grant Number NBS(G)	Title of Project	Principal Investigator	NBS Monitor and Division	Funds Committed Basic Grant (k$)	Page(s)
18	The investigation of the decay of even-even nuclei in the medium weight region.	P. Trehan	R.S. Caswell 240	72.4	46
30	Transport properties of solids at low temperatures-	G.S. Verma	A. Kahn 313	9.2	95
34	Investigations in the chemical and thermodynamic properties of refractory materials.	V. V. Dadape	W.S. Horton 313	125.0	70
40	Gamma ray scattering	P. P. Kane	J. W. Motz 243	7.1	120
41	Properties of electrolytes in nonaqueous media	M. N. Das K. K. Kundu	R. A. Durst 310	48.0	9
47	Investigations on molecular spectra	N. L. Singh	A. Bass 316	65.0	34
49	Studies of the electrical breakdown at the junction of metals and solid dielectrics in high vacuum at high voltage.	H.Gopalakrishna	F. R. Kotter 211	24.1	107
50	Electrical behavior of pure and doped oxides and other ionic solids.	E.C. Subbarao	R.S. Roth 313	21.5	82
51	Studies of the thermodynamic properties of amorphous, disordered and defect oxides.	C.N.R. Rao	H.F.McMurdie 313 H.S. Peiser 156	38.0	27
57	Investigation on the interaction on gamma rays with matter	A.M. Ghose	E. G. Fuller 240	42.1	116

APPENDIX III

LIST OF SFCP GRANTS IN INDIA

Grant Number NBS(G)	Title of Project	Principal Investigator	NBS Monitor and Division	Funds Committed Basic Grant (k$)	Page(s)
66	Point defects in alkali halides.	S.C. Jain	L. H. Gevantman 151	12.6	18
77	Critical reviews of phase transformation in inorganic solids.	C.N.R. Rao	L.H. Gevantman 151	7.0	24
78	Infrared bibliography.	C.N.R. Rao	L.H. Gevantman 151	12.7	26
89	Glass and ceramic chemical composition - SRM Program.	S. Kumar	O. Menis 310	8.0	58
91	Composite structural systems in buildings.	J.K. Sridhar Rao	E.O. Pfrang 460	31.0	102
92	Preparation of standard reference materials of ferro-alloys.	V. A. Altekar	R. E. Michaelis 302	32.3	55
99	Study of structural elements under dynamic loading.	V. Sundararajan	E. O. Pfrang 460	16.5	105
114	Physical and thermodynamic properties of halogenated alkanes.	A.P. Kudchadker	H. J. White 151	56.7	21
126	Experimental investigations on the generalized optical model parameters of fast neutrons.	A. M. Ghose	R. B. Schwartz 243	38.0	113
127	Magnetic properties of atomic nuclei and of the nuclear environment and on the life-times of nuclear states.	G.N. Rao	L.H. Gevantman 151	29.6	30

APPENDIX III

LIST OF SFCP GRANTS IN INDIA

Grant Number NBS(G)	Title of Project	Principal Investigator	NBS Monitor and Division	Funds Committed Basic Grant (k$)	Page(s)
132	Platinum group metal complexes their preparation, structure and role in homogeneous catalysis.	M. M. Taqui Khan	T. D. Coyle 313	8.2	77
133	Study of transition metal oxides with special reference to their catalytic properties	V. C. Sastri	R. Klein 316	14.0	64
144	Low temperature and high pressure x-ray investigations of phase transitions.	K. V. Krishna Rao	S. Block 313	16.0	60
163	Optical spectra of simple molecules.	P. Venkateswarlu	A. Bass 316	20.0	51
166	Gamma ray scattering.	P. P. Kane	J. H. Hubbell 240	30.6	12
167	Review of physical properties of alloys.	S. K. Joshi	D. Kahan 312	27.0	19
172	Development of high pressure techniques and some applications.	R. S. Krishnan	P.L.M. Heydemann 221	26.0	7
174	Ultrasonic dispersion and absorption.	S. K. Kor	M. D. Scheer 316	17.0	5
175.	Catalytic high pressure hydrogen transfer reactions.	C. N. Pillai	R. Klein 316	15.0	63

APPENDIX IV

ALPHABETIC LIST OF NBS MONITORS

NBS Monitor	Division	Page(s)
Bass, A.	316	34, 51
Bates, R. G.	310	9
Bennett, H. S.	310	82
Block, S.	313	60
Caswell, R. S.	240	46
Coyle, T. D.	313	77
Durst, R. A.	310	9
Fuller, E. G.	241	116
Gevantman, L. H.	151	18, 24, 26, 30
Heydemann, P.L.M.	221	7
Horton, W. S.	313	70
Hubbell, J. H.	240	116, 122
Kahan, D.	312	19
Kahn, A.	313	95
Klein, R.	316	63, 64
Kotter, F. R.	211	107
McMurdie, H.F.	313	27
Menis, O.	310	58
Michaelis, R. E.	302	55
Motz, J. W.	243	120
Peiser, H. S.	156	27
Pfrang, E. O.	460	102, 105
Roth, R. S.	313	82
Scheer, M. D.	316	5
Schwartz, R. B.	240	113
Taylor, J. K.	310	9
Wachtman, J. B.	313	82
White, H. J.	151	21

APPENDIX V

ALPHABETIC LIST OF PRINCIPAL INVESTIGATORS

APPENDIX VI

INDEX OF INSTITUTES

☆ U. S. GOVERNMENT PRINTING OFFICE : 1973--542-650/72

FORM NBS-114A (1-71)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBS TN-798	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

Collaborative Research Program Between NBS and Indian Scientific Institutions

NBS Special Foreign Currency Program 1973 Status

5. Publication Date
November 1973

6. Performing Organization Code

7. AUTHOR(S)
H.Steffen Peiser, Michael B. McNeil, Doris M.Bluebond

8. Performing Organization

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address
Same as 9.

13. Type of Report & Period Covered
Final

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

An overview is given of grants awarded by the National Bureau of Standards under the Special Foreign Currency Program in India, authorized by Public Law 480 and its amendments. Each grant is identified by title, principal investigator, institution in India, NBS monitor charged with working in close technical touch with the project in India, and the monitor's organizational unit within NBS. The relevant work is then described briefly under the three headings "Summary Description of Project Goals," "Results and Implications to Date," and "List of Publications that Resulted from the Project." To demonstrate the wide use of such grants over the entire Program Structure of NBS, the grant descriptions are ordered by the elements of that Program Structure. Editorial comment on the significance and purpose of the NBS/SFCP grant program is confined to a Foreword and Introduction. The editors judge this grant program to have had a high benefit to cost ratio from the viewpoint of NBS.

17. KEY WORDS (Alphabetical order, separated by semicolons) Binational research cooperation; international scientific cooperation; India science and technology; physical science research administration; research planning; scientific research abstracts; Special Foreign Currency Program.

18. AVAILABILITY STATEMENT

☒ UNLIMITED.

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19. SECURITY CLASS (THIS REPORT)
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20. SECURITY CLASS (THIS PAGE)
UNCLASSIFIED

21. NO. OF PAGES
139

22. Price
$1.50

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