

# NATIONAL BUREAU OF STANDARDS

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**RESEARCH ON CRYSTAL GROWTH  
AND CHARACTERIZATION AT THE  
NATIONAL BUREAU OF STANDARDS  
DURING THE PERIOD JANUARY TO JUNE 1963**

Edited by H. Steffen Peiser  
National Bureau of Standards

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

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Abstract

The National Bureau of Standards with partial support from the Advanced Research Projects Agency is continuing diverse research projects on the growth and characterization of crystals. This note summarizes the individual NBS activities in this and closely related fields during January to July 1963. Lists of NBS publications appertaining to that period and of participating NBS scientists are appended.

1. INTRODUCTION

This is the second biannual collection of brief statements on research in progress at the National Bureau of Standards on crystal growth and characterization. In the previous collection the general purpose, background, and program area have been described (see NBS Technical Note 174 issued on March 15, 1963). Much of the research now summarized has again been supported directly from NBS funds, but an increasing proportion has been financed by transferred funds from the Advanced Research Projects Agency. This assistance from ARPA has made a great deal of difference, especially in encouraging the rapid expansion of promising projects. This help is hereby gratefully acknowledged, but in the text no attempt has been made to single out the particular portions of the work that have been ARPA supported. Only where other agencies have made additional funds available a separate acknowledgment is given.

The research statements have been edited and assembled with the invaluable help of assistant editors from the NBS organizational divisions as follows:

|                                    |                     |
|------------------------------------|---------------------|
| Electricity:                       | J. D. Hoffman       |
| Heat:                              | J. F. Schooley      |
| Analytical and Inorganic Chemistry | L. J. Frolen        |
| Mechanics:                         | R. S. Marvin        |
| Polymer:                           | E. Passaglia        |
| Metallurgy:                        | R. L. Parker        |
| Inorganic Solids:                  | F. A. Mauer         |
| Atomic Physics:                    | H. P. R. Frederikse |
| Instrumentation:                   | J. C. French        |
| Physical Chemistry:                | D. E. Mann          |

The collaboration of the NBS Boulder Laboratories is greatly welcomed. Mrs. E. Burnette and Miss R. M. Delaney have also helped in the assembly of the material. B. Paretzkin assisted in the selection and preparation of figures.

The decisions regarding inclusion or exclusion of statements from the diverse research projects have been left to the discretion of project leaders, division editors, and division chiefs, but in general encouragement has been given to participate in the writing of this report even where such critical border subjects are involved as crystal-surface studies, crystal-phase equilibria, crystal-structure determinations, etc. The program area delineated by this report is therefore slightly wider than that defined in NBS Technical Note 174 Section 3.

The summaries are now grouped into four sections as follows:- Crystal Growth, Defect Characterization, Crystal Physical Properties, and Crystal Chemistry. The areas covered are defined at the beginning of each section. Many individual statements might well have fitted into more than one of these broad categories. The order within sections has not been logically justified. It is indeed a good feature of the crystal program at NBS that the cross-links between projects are so numerous that there can be no completely satisfactory order of presentation.

The ARPA "Crystal Group" at NBS has sponsored a number of activities during the first half of 1963. There have been monthly evening colloquia on specific topics. Many well attended colloquia have also taken place to mark visits of crystal scientists from other research institutes. To a symposium on the general topic of "Research Programs in Crystal Growth and Defect Characterization" NBS and ARPA invited about seventy scientists from many U. S. laboratories. NBS scientists have visited and corresponded with many other interested laboratories.

Thus the NBS "Crystal Group" by individual effort coupled with good collaboration aims to contribute significantly to a field of science that presents many opportunities for fundamental progress. No one doubts the importance of the technological advances that ultimately will follow such progress.

## 2. Crystal Growth

Contributions to this section are concerned with mechanisms and techniques of crystal growth and dissolution of single crystals.

### 2.1. High-Temperature Crystal Growth<sup>\*</sup>

W. S. Brower and F. Ordway,

Crystal Growth Section

The primary purpose of this project is to investigate the influence of growth parameters on the perfection of refractory oxide crystals with the ultimate aim of developing techniques for growing more nearly perfect crystals of high-melting compounds as typified by rutile,  $\text{TiO}_2$ ; sapphire,  $\text{Al}_2\text{O}_3$ ;  $\text{Cr}_2\text{O}_3$ ; and stabilized  $\text{ZrO}_2$ .

Temperature measurements have been made using Ir-IrRh thermocouples while growing crystals of sapphire by the Verneuil process. Measurements are now being made incorporating some refinements of technique.

Crystals of rutile grown at widely varying rates are being examined by the etch technique to determine the effect of growth rate on the character of the sub-grain boundaries and the average dislocation densities.

A new flame-fusion burner was designed which will permit the use of acetylene or acetylene-hydrogen mixtures, thus extending the temperature range of the conventional flame-fusion assembly.

A high-frequency RF generator (30 - 150 Mc) has been purchased. It will be used both in attempts to grow crystals of some of the oxides using direct coupled RF power, and as the power source for the inductively coupled plasma torch. The machine will be incorporated into the present program and the crystals produced will be evaluated with respect to those produced by other methods.

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

## 2.2. Crystal Growth and Structure Studies

D. E. Roberts and M. I. Cohen,  
Solid-State Physics Section

The emphasis has been on the growth of cadmium telluride, CdTe, crystals. First the elements are reacted; this process is complicated by the high heat of reaction and by the high vapor pressure of the components. Subsequently the compound is melted into one end of a tube; the dead space is filled with a quartz plug before sealing the tube at the other end. (This method originally described by Lorenz and Halsted of the General Electric Laboratories maintains the stoichiometry of the compound.) After lowering the tube through a heated zone an ingot is obtained which contains single crystals as large as 1 cm across. So far all ingots prepared in this way are p-type.

The growth of rutile,  $\text{TiO}_2$ , crystals by the Verneuil technique is continued; boules with one of about 15 different doping agents have been prepared.

A large portion of the effort has been expended on orientation studies of crystals, among them  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ , spinel,  $\text{PbF}_2$ ,  $\text{MnF}_2$ ,  $\text{KN}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and PbS.

Samples of  $\text{TiO}_2$  that had been subjected to uniaxial pressures of 50 kbars and 100 kbars were examined. No changes could be detected.

The variable-temperatures (range  $-175^\circ\text{C}$  to about  $2100^\circ\text{C}$ ) attachment for the X-ray diffractometer has been installed and preliminary tests made.

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

T. H. Orem, Metal Reactions Section;

R. L. Parker and H. C. Vacher,  
Metal Physics Section

For background see the description in NBS Technical Note 174 Section 4.3. The crystal puller has been received and put into operation. A suitable power supply, temperature control, and gas supply were set up. Several aluminum crystals were pulled from 5-9 purity aluminum, in a helium atmosphere. By suitable control of melt temperature and pulling speed, Al single crystal rods less than 1 mm in diameter were grown. The seeds used had been grown by the Bridgman technique. Laue back-reflection X-ray photographs showed that the pulled crystals had fewer imperfections than the seed crystals. High-voltage Laue transmission studies were also made.

A Rigaku-Denki microfocuss X-ray diffraction unit has been put into operation in cooperation with the Physical Properties Section. The Lang camera for this unit has not yet arrived. Preliminary studies have been started using divergent-beam methods (pseudo-Kossel lines).

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

J. G. Early and R. L. Parker,  
Metal Physics Section

For background see the description in NBS Technical Note 174 Section 4.4. Visits to Drs. Tiller and Kramer at Westinghouse Research Laboratories have been made and plans to set up apparatus similar to theirs are proceeding. It was learned that their method [described theoretically in J. Chem. Phys. 37, p. 841 (1962)] has provided measurements of interface temperature in the growth of metal crystals from the melt.

## 2.5. Crystal Growth from Solution

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

The objectives of this project (see also NBS Technical Note 174 Section 4.5) concern (a) the development of crystallization techniques for the growth of large single crystals and the preparation of single-crystal specimens of inorganic and organic substances; (b) studies of the properties of single crystals, both those of high purity and those containing selected impurities, by appropriate physical and chemical methods; and (c) basic research relating to the mechanisms of crystal growth and impurity retention.

Single-crystal growth from aqueous solution by temperature-program techniques has continued the production of specimens of ammonium dihydrogen phosphate (pure and containing chromium impurity), sodium chlorate (pure and containing copper impurity), sodium nitrate, and potassium chloride. Individual recorders, presently on order, are to be incorporated and an automatic warning system for temperature-control failure will be included.

With some revisions of a design proposed by Karpenko, et al. [Sov. Phys. Cryst. 6, No. 1, 120 (1961)], apparatus for the growth of single crystals from solution by evaporation and circulation of the solvent has been constructed. The equipment is to be used for crystal growth at constant temperature and is expected to be particularly effective for those substances having low temperature coefficients of solubility. Experiments on the adequate control of temperature are in progress.

Solvent effects on the growth of large single crystals from solution have been strikingly illustrated in experiments with oxalic acid. The anhydrous acid crystallizes from glacial acetic acid solution to give single-crystal specimens of inferior quality containing inclusions of mother liquor. The addition of small amounts of water to the solvent promotes the growth of single crystals of greatly improved quality. A phase study of the system oxalic acid/acetic acid/water at 50°C has shown anhydrous oxalic acid to be the stable solid phase in equilibrium with acetic acid/water solutions containing up to 5.2 percent water (J. Strassburger and J. L. Torgesen, 1963).

Good single crystals of oxalic acid dihydrate are difficult to grow from water solution. Inferior specimens, growing primarily by deposition on {001} with a resultant habit in which {101} and {110} predominate, are cloudy with inclusions of mother liquor. Growth from solution in acetone/water mixtures produces specimens with marked improvement in crystal quality. Deposition occurs primarily on {110}. The habit becomes increasingly prismatic at higher acetone concentrations with {001}, {101}, and {110} predominating. Details of these studies on oxalic-acid crystal growth will be submitted for publication.

Other steady-state diffusion processes for the growth of single crystals of sparingly soluble salts have been abandoned in favor of growth in silica gel. Although initial experiments have been confined principally to a duplication of conditions described by Holmes [J. Franklin Inst. 184, 743 (1917)], some effects of gel acidity, and the nature and concentration of reacting and foreign ions have been observed. Successful results have been obtained with lead iodide (hexagonal platelets 4-5 mm wide and 1 mm thick), copper tartrate (well-developed habit, 3 mm long and 1/2 mm in diameter), and calcium sulfate dihydrate (gypsum). Small crystals of mercuric iodide, silver dichromate, and lead chromate have been grown, but little success has been achieved with silver halides.

Completely satisfactory results have not been obtained in the preparation of thin sections of water soluble substances for dislocation studies by etching and X-ray diffraction microscopy. The most promising final step in surface preparation appears to be a general "chemical" etch by agents having low to moderate solvent action.

## 2.6. The Crystallization of Polymers from Concentrated Solutions

F. Khoury, Polymer Physics Section

It is well established that crystallization in the spherulitic form occurs most





Figure 1. Individual polypropylene spherulites grown from a 10% solution of the polymer in xylene. The spherulites are shown as seen after evaporation of the solvent. (Unpolarized oblique incident illumination x 400).

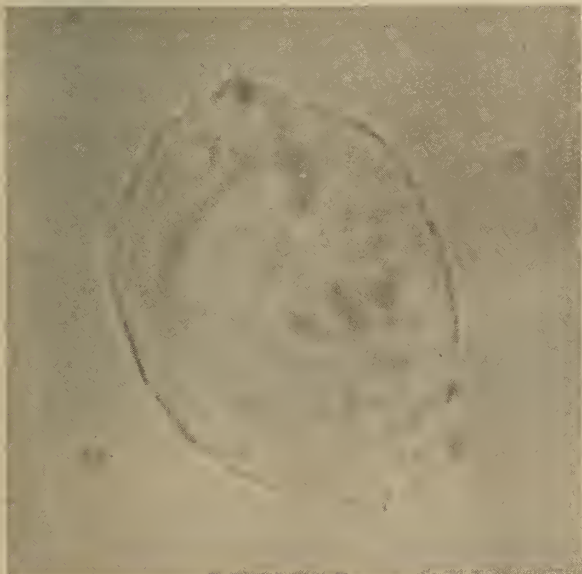


Figure 2. Three dimensionally asymmetric aggregates of polypropylene grown from a 0.75% solution of the polymer in paraffin oil. Aggregate is in suspension in solvent and is depicted as seen oriented such as to occupy a maximum surface area in the field of the microscope. (Unpolarized light x 2000).



Figure 3. Sheaflike appearance which is characteristically seen when an aggregate of the type shown in figure 2 is rotated through  $90^\circ$  about any axis in the plane of the microscope stage. (Unpolarized light x 2000).



Figure 4. Spherulite of polyhexamethylene adipamide (66 nylon) grown from a 10% solution of the polymer in glycerol. The spherulite is in suspension in the solvent. (Crossed Nicols x 1500).

commonly when synthetic polymers are crystallized from the melt. Much attention has been directed in recent years to the determination of the morphology of polymer spherulites. In view of the inaccessibility of the latter aggregates in bulk polymer most investigations have been confined to a study of spherulites formed in thin polymer films. By essentially restricting the growth of the spherulites to two dimensions within the plane of these films, and subsequently replicating the surface of the films for examination under the electron microscope, a cross-sectional rendition has been obtained of the morphology of spherulites of various polymers.

In order to elucidate further the mechanisms of growth of polymer spherulites, one would wish to supplement such studies as have been mentioned above by an investigation of the surface morphology of spherulites (quenched at various stages of development) whose growth from the melt has not been restricted by sample geometry. The experimental barriers to such a study would be overwhelming, if not insurmountable.

During the course of a recent investigation of the crystallization of polypropylene from hot, moderately concentrated solutions (1-10%) of the polymer in various solvents (e.g. xylene, decalin, paraffin oil) it has been found that, on cooling, such solutions yield polymer spherulites in suspension in the solvent (Fig. 1). By varying the concentration of polymer, the solvent used, or the rate of cooling, spherulites have been obtained which exhibit different signs of radial birefringence and apparent coarseness of internal texture.

Under certain circumstances, in particular on crystallization of polypropylene from mineral oil, individual polymer solutions have been found to yield in addition to spherulites a variety of crystalline aggregates which exhibit three-dimensionally asymmetric growth patterns- they thus present distinctly different appearances when viewed under the optical microscope, depending on their orientation in the field of view. An example typical of many such asymmetric aggregates is shown in figure 2. Characteristically, when they are oriented so as to occupy a maximum surface area in the field of view of the microscope, they exhibit a roughly elliptical shape, as may be seen in figure 2. If, however, they are rotated from this position through  $90^\circ$  about an axis in the plane of the microscope stage they appear sheaflike in shape (Fig. 3). The nature of the fine structure of these and other related types of asymmetric aggregates which have been observed is as yet unknown. Replicating techniques in conjunction with electron microscopy will be applied to determine in detail the nature of their morphology and associated growth processes. Although their various asymmetric structures are in themselves of interest they are also of further interest since it has been found that their various habits are similar to those of the successive structures which develop during the early stages of growth of individual spherulites from polypropylene solutions in paraffin oil. Briefly, therefore, conditions have been found which yield polypropylene aggregates in suspension in solvent which are representative of the various stages of growth of polymer spherulites. These various aggregates can be readily isolated and replicated for electron microscopy. Such an investigation should provide detailed information on the mechanism of growth (e.g. the role played by crystal imperfections and non-crystallographic branching) of spherulites from solution which would also be pertinent to a better understanding of the formation of spherulites in bulk polymer when it is crystallized from the melt.

Similar studies are being extended to other polymers, in particular 6-nylon and 66-nylon which we have recently crystallized from solution in the form of spherulites (Fig. 4) as well as sheaf-like aggregates.

## 2.7. Crystallization of Polyethylene Fractions

R. C. Neuman, Dielectrics Section

and J. Powers, Macromolecules Synthesis and Structure Section

The morphology of polyethylene fractions with a molecular weight between 1800 to  $1.4 \times 10^6$  was examined over a range of crystallization temperatures from  $100^\circ\text{C}$  to  $131^\circ\text{C}$ . A densely granulated field usually resulted for most fractions at most temperatures. For a few samples ringed spherulites were discerned in the crystallization temperature range from

100°C to 115°C, but these appeared too rapidly (20-30 sec) for measurements of their growth rate to be made. The ring spacing was found to increase with increasing crystallization temperature. These samples melt at temperatures from 126°C to 128°C, well below the usual polyethylene melting temperature of 136°C to 138°C. Subsequent crystallization in the temperature range 127°C to 131°C produced a granulated field. The variables studied included temperatures above the melting point at which the sample was melted, temperatures of crystallization, and whether the sample was melted and crystallized on the Kofler hot stage, or in silicone-oil baths. The high nucleation rate indicates polyethylene is wetted by a number of heterogeneous nuclei, such as cellulose. Some samples, cleaned by precipitation techniques, showed no differences in structure or growth rate from uncleaned samples.

## 2.8. Homogeneous Nucleation in Polymer Crystallization

### F. Gornick, Macromolecules Synthesis and Structure Section;

Lois Frolen and Gaylon Ross, Pure Substances Section

Precise measurements of homogeneous-nucleation rate constants is desired in order to test and enlarge upon existing theories relating such constants to other measurable properties of polymers and other materials. The most effective means of obtaining truly homogeneous nucleation rates is by the droplet method, i.e., by subdividing a purified liquid into droplets small enough that most of them will be free of nucleation catalysts. The temperature coefficient of nucleation of these droplets is then measured. In polyethylene it is desired to measure the nucleation rate over a very wide temperature range. Apparatus for the production of spherical droplets of purified fractions of polyethylene is under development. The apparatus has been designed to produce droplets ranging from one to ten microns in diameter. Special microscope accessories such as ultra-long range objectives and a hot stage with precise temperature-measurement capability are under design. This equipment will permit the measurement of nucleation rates of polyethylene under isothermal conditions, this system having been studied by other investigators under non-isothermal conditions. The studies can be extended to other substances, such as a group of well purified di-phenyl alkanes that are available.

## 2.9. Vapor-Phase Growth Kinetics of Metal Crystals

R. L. Parker, Metal Physics Section

For background see the description in NBS Technical Note 174 Section 4.8.

The mass spectrometer has been ordered but not yet received. Part of the present apparatus has been used in experiments described in 4.16.

## 2.10. Crystal Growth by Electrodeposition

F. Ogburn, Electrolysis and Metal Deposition Section

For background see the description in NBS Technical Note 174 Section 4.9.

X-ray examination by the Buerger and Weissenberg methods has shown 5-fold symmetry, of copper dendrites grown electrolytically, about the growth axis parallel to [110]. This is thought to be due to a series of twins in the dendrite. In another set of dendrites of Cu, optical metallographic examination showed pairs of twin planes extending through dendrite branches, indicating that twinning may play a role in branching. Lead dendrites have been grown electrolytically and are being examined.

## 2.11. Stress-Induced Martensitic Transformations

R. P. Reed and C. J. Guntner,  
Cryogenic Engineering Laboratory

A commercial 18% chromium-8% nickel iron alloy was examined in tension at 300, 76, 20, and 4°K. Continuous stress-strain recordings were made, X-ray analyses at periodic stress

(strain) intervals were obtained, and magnetic measurements were taken. From this data the percentages of martensitic products ( $BCC_{(\alpha)}$  and  $HCP_{(\epsilon)}$ ) were computed as a function of stress (strain).

It was found that up to 15%  $\epsilon$  phase forms at low temperatures. The amount of  $\epsilon$  formed increases to about 5% strain, then decreases. This decrease indicates the additional transformation of  $\epsilon$  to  $\alpha'$ . The total amount of  $\epsilon$  and  $\alpha'$  was suppressed at constant stress (strain) at 4°K as compared to that at 76°K. It is proposed that the suppression of  $\epsilon$  and  $\alpha'$  is associated with the decreased mobility of extended dislocations at very low temperatures. The yield strength decreased as the temperature was depressed below room temperature and then increased rapidly near 4°K.

## 2.12. Radio-Materials Synthesis

P. M. Gruzensky,

Radio and Microwave Materials Section

Efforts to determine the optimum conditions for synthesis of anhydrous copper sulfate and zinc sulfate doped with copper have continued during this report period. A sulfuric acid-ammonium sulfate mixture has been used as solvent, as reported previously, and offers some advantages over the separate components. Some preliminary experiments indicate that the crystal habit can be changed by adding a small amount of an alkali metal sulfate to the solvent. Additional experiments are indicated and will continue.

The low nuclear magnetic moment, as well as the trigonal structure, of calcite make it of interest as a host structure for paramagnetic ions in resonance studies. Unfortunately, to date sizeable crystals of this material have defied synthesis and only those paramagnetic impurities which exist in natural calcite specimens have been examined. Experiments in this laboratory have been concentrated on synthesis by a slow diffusion of carbonate ion through a solution containing a calcium salt. Optical-quality rhombs with edge dimensions up to 1 mm have been obtained in this way but obvious flaws develop as the crystals grow larger. In future work, considerable attention will be given to the purification of starting materials in an effort to reduce the number of nucleation centers.

It is anticipated that the synthesis of lead sulfide single crystals will be given some consideration in the future. Artificial crystals of this material have been prepared by others using the Bridgman technique, but these crystals deviate from stoichiometry as a result of partial decomposition at the high temperatures involved. A crystal-growth technique at lower temperatures would be a contribution in the study of intrinsic properties in PbS.

## 2.13. Thermal Etching of Crystalline Argon

G. L. Pollack and E. N. Farabaugh,

Crystal Growth Section

Reliable experimental tests of many theoretically predicted properties of solid rare gases can best be made on large single crystals. By successive freezing from the melt, a modified Bridgman method, crystals of argon have been grown near the triple point with about centimeter dimensions as revealed by thermal etching (Pollack and Farabaugh, 1963). Techniques of growth and etching at different temperatures and pressures have been developed and investigated. Crystal-growth rate and size have been examined as functions of temperature gradient, supersaturation, and chamber geometry, and have been related to modern theories. Interesting comparisons can be drawn between the mechanism of thermal etching in a system of low surface energy and high triple-point vapor pressure, such as crystalline Ar, and the same process in metals which has been studied often. Many surprising details on the crystal surfaces have been observed; striations and what may be rosettes have been examined. Experiments which were not possible before are now practical with these crystals and are being investigated. The techniques of crystal growth and etching are being extended to other rare gases and molecular solids.

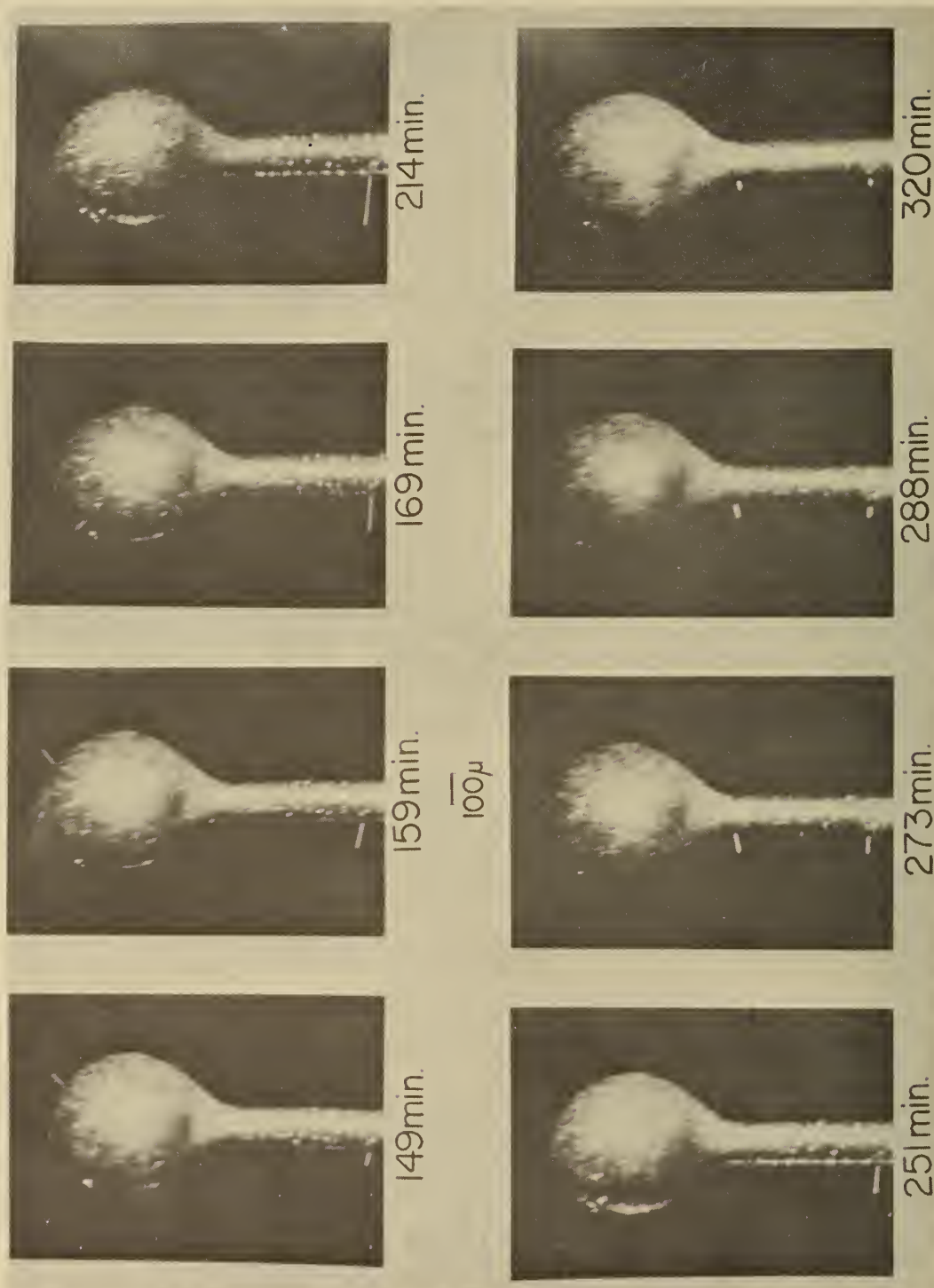


Figure 5. Growth and Evaporation of Potassium Whiskers at 53°C.  
 (Observe whisker at lower left of pictures)

## 2.14. Whisker Growth of Rare Gases

G. L. Pollack,

Crystal Growth Section

Preliminary experiments have been performed to determine the conditions under which whisker growth of rare-gas crystals will occur and to measure properties of the whiskers. Dendritic growth from the melt has already been observed and investigated (Pollack and Broida, 1963a). Vapor-deposition studies at temperatures between 77°K and 20°K and at pressures from 0.5 atmosphere down to 10 microns have demonstrated the possibility of growing whiskers from the vapor and measuring their length as a function of time. These experiments are aimed at advancing theories of surface properties, and especially surface mobilities, by looking at the prototype rare-gas solid surfaces.

## 2.15. Kinetics of Whisker Evaporation

R. L. Parker, R. L. Anderson, and T. Wagner,

Metal Physics Section

For background see the description in NBS Technical Note 174 Section 4.16.

We have studied both the growth and the evaporation of potassium and mercury whiskers and have found that the surface-diffusion equation can quantitatively account for many aspects of both growth and evaporation in these systems. The whiskers are nucleated and grow on silver or tungsten substrates in pure, supersaturated metal vapor in a sealed-off pyrex vessel, prepared by ultra-high-vacuum techniques. Direct optical measurements of the whisker length as a function of time for various temperatures and supersaturations were made. Some two thousand photographs have been taken; figure 5 shows a typical sequence for potassium whiskers.

From the surface-diffusion equation,

$$(1) \quad D \frac{\partial^2 c}{\partial x^2} - \frac{c}{\tau} + N = \frac{\partial c}{\partial t}$$

where  $x$  is distance from the whisker base,  $c$  the adatom surface concentration,  $N$  the incident vapor flux,  $D$  the surface diffusion coefficient, and  $1/\tau$  the evaporation probability, one obtains the following equation for the whisker length  $\ell$ , assuming a steady-state growth process and appropriate boundary conditions:

$$(2) \quad \frac{d\ell}{dt} = K(N - N_0) \frac{\lambda}{r} \tanh\left(\frac{\ell}{\lambda}\right)$$

Here  $K$  is a known constant,  $r$  the effective whisker radius,  $N_0$  the equilibrium flux, and  $\lambda = \sqrt{D\tau}$ . This equation predicts, in the case of growth ( $N > N_0$ ), an initial exponential increase in length, followed by a linear increase in length. We have observed both regions optically on K and Hg whiskers, and have obtained  $\lambda$  and  $r$  values for these whiskers. A typical  $\lambda$  value for K at 55°C is 60 microns. If now one takes the case of evaporation ( $N < N_0$ ), the same equation (2) predicts, if the same mechanisms are operating during evaporation as during growth, first a linear decrease in length and then an exponential decrease. Again, we have observed both regions optically on K and on Hg whiskers (R. L. Anderson and R. L. Parker, 1963). Further studies on these whiskers are continuing.

## 2.16. Theoretical Studies in Whisker Crystal Growth

J. S. Simmons, R. E. Howard, and R. L. Parker,

Metal Physics Section

and H. J. Oser, Computation Section

For background see the description in NBS Technical Note 174 Section 4.17.

An implicit exact solution for the time-dependent surface-diffusion equation describing the general case of whisker growth with re-evaporation has been obtained. This solution assumes that the surface concentration tends to zero near the whisker tip. It is hoped eventually to remove this restriction.

Using the principle of conservation of mass, an auxiliary integral equation has been obtained; it appears suitable for machine computation of the non-linear system governing whisker growth. This computation procedure has been programmed and the program is currently being checked prior to a production run on the IBM 7090 computer.

Asymptotic solutions have been obtained for both short and long times. In this general case, for long times, the length becomes linear in time. Finally, the growth equations can be dimensionalized so as to reduce the problem to a one-parameter family of curves governed by a reduced evaporation parameter  $\tau'$ .

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

S. C. Hardy and R. L. Parker,  
Metal Physics Section

Field-emission patterns of potassium whiskers taken during growth do not show the dark areas corresponding to crystal planes of high work function which are usually seen with other metals. We have tentatively attributed this to the sputtering and consequent roughening of the whisker tip by ions formed in the K vapor by electron impact. We have obtained symmetric patterns from K whiskers by reducing the vapor pressure to a low value before application of the field. These patterns are characteristic of bcc emitters with  $\{110\}$  orientation but do not display any fine structure.

Several F.E. tubes designed to study the heterogeneous nucleation of mercury on tungsten have been built.

#### 2.18. Field-Emission Studies

W. J. Ambs and E. Escalante,  
Metal Reactions Section

For background see the description in NBS Technical Note 174 Section 5.22.

The adsorption of oxygen at room temperature on a clean nickel surface has been found to depend strongly on crystal face, showing considerable enhancement of emission on planes close to  $\{110\}$ . Adsorption at 77°K shows no such phenomenon.

Preliminary experiments on iron show that iron whiskers can be grown by heating iron field emitters to 900°C in the electric field. The phase transition at 910°C has also been observed.

Experiments have been started on the growth and oxidation of magnesium films deposited on tungsten. The purpose is to check the validity of proposed oxidation mechanisms involving "island nuclei."

#### 2.19. Studies of Small Crystals of Nickel and Nickel Halides

D. R. Winder, Radio and Microwave Materials Section

Nickel whiskers, nickel halide whiskers and platelets have been grown for studies of dimensionality in magnetism. The conditions for growth of these crystals have been studied and the growth characteristics of the platelet habit investigated. A paper by E. N. Sickafus and D. R. Winder on the last subject was presented at the Colorado-Wyoming Academy



of Science, May, 1963. The abstract follows:

"Hydrated crystals of  $\text{NiBr}_2$  have been grown in the relatively cool, downstream end of the whisker growth chamber during the growth of Ni whiskers by the method of hydrogen reduction of the halide. These crystals are in the form of platelets and very thin dendrites. The dendrites grow first and then growth spirals occur on the dendrites which produce a heavy overgrowth and usually cover up most of the original dendritic structure. The growth spirals have relatively large steps (several hundred angstroms) and are easily resolved with the optical microscope. Double beam interference patterns are presented which have been made under monochromatic illumination."

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

T. H. Orem, Metal Reactions Section

For background see the description in NBS Technical Note 174 Section 4.19.

In recent studies of the relationship between oxide film and substrate on aluminum, the configurations of what are currently considered to be pits caused by vacancy condensation have been investigated. The pit edges are often parallel to traces of close-packed planes in the surface in question. Pits in other crystallographic surfaces are being investigated.

## 2.21. Thermal Evaporation from $\{0001\}$ Zinc Surfaces

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

The purpose of this research was to investigate the surface structures developed during thermal evaporation from freshly cleaved zinc single crystals. Particular attention was devoted to the role of pre-existing surface steps, dislocations, surface impurities and volume impurities. Typically, the surface to be studied was held at  $300^\circ\text{C}$  for 15 minutes in different controlled vapor undersaturations from  $(p/p_0) = 0.80$  to  $0.006$ , either in a residual vacuum of about  $1 \times 10^{-8}$  torr. or in an oxygen environment up to pressures of  $3 \times 10^{-5}$  torr.

Under these conditions, evaporation pits were produced at either pre-existing steps or flat-surface regions. A critical undersaturation ratio of  $0.29$  was required to produce these features, which persisted to the lowest undersaturation employed. The number density of the evaporation pits did not vary with undersaturation in this range, being about  $4 \times 10^4 \text{ cm}^{-2}$ . The average dislocation density in the same samples, determined by chemical etching methods was  $3 \times 10^4 \text{ cm}^{-2}$ . This fact, combined with observations on evaporated matched cleavage surfaces, lead to the conclusion that dislocations were particularly effective in nucleating the evaporation pits. Interferometric pit-slope measurements showed the slopes increased with increasing undersaturation and with increasing surface-impurity concentration. There was no apparent effect on varying the bulk-sample purity between  $99.9\%$  and  $99.998\%$ .

The results are in agreement with some aspects of the theory of surface evaporation from dislocation sites, but indicate the need for a quantitative treatment of dislocation-core effects and impurity effects. High resolution electron-microscope surface studies indicated very complex step configurations, both near and away from the step sources (See Fig. 6.).



Figure 6. Electron micrograph of a shadowed carbon replica from a thermally evaporated {0001} zinc surface, illustrating the step structure at evaporation pits. Magnification = 4400.

### 3. Defect Characterization

Contributions to this section are concerned with studies of defect- or dislocation-sensitive properties of single crystals

#### 3.1. Studies of Crystal Defects

D. J. Barber and N. J. Tighe,  
Physical Properties Section

As part of a study of the mechanical behavior and defect properties of oxide materials (Barber, 1963; Barber and Tighe, 1963), specimens thinned from bulk samples of synthetic sapphire, ruby, and "star" sapphire, have been examined by transmission electron microscopy. Glide elements for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> system have been confirmed but, in addition, dislocation loops have been found which lie in the {0001} plane and have their Burgers vector in the c-direction. There is some evidence for the occurrence of precipitates in ruby; TiO<sub>2</sub> precipitates in "star" sapphire have been examined but no associated dislocation configurations have been seen. Further work will be carried out using a hot stage in the microscope.

In further work on materials with the rutile structure, magnesium fluoride, MgF<sub>2</sub>, crystals have been thinned by ultrasonic drilling and subsequent polishing in hot sulfuric acid.

In the electron microscope the crystals suffer beam damage; many small dislocation loops appear, and these grow and interact. The loops will be studied in detail to determine their character. Cobalt fluoride, CoF<sub>2</sub>, which also possesses the rutile structure, does not exhibit damage at comparable beam intensities.

#### 3.2. Defects in Thin Oxide Films

J. Kruger, H. T. Yolken, and J. P. Calvert,  
Metal Reactions Section

These studies are concerned with the role of defects in thin oxide films in the kinetics of growth and decay. They consist of:

- a) A study of the role of crystal orientation and of dislocations on the sites of passive film breakdown. (J. Kruger, 1963).
- b) Optical studies of strain in thin oxide films formed on iron and copper single-crystal surfaces, and electron-diffraction studies of the epitaxial relationships between film and substrate.

#### 3.3. Surface Structure of Vapor-Grown Crystals

R. L. Parker, Metal Physics Section

For background see the description in NBS Technical Note 174 Section 5.23.

Professor A. R. Verma, Varanasi, India, has examined some cadmium platelets grown at NBS from the vapor. Because of their small size (~0.2 mm diameter) and rather firm attachment to the curved walls of the growth vessel, it proved to be difficult to mount the crystals properly for multiple-beam interferometry. Larger platelets will be grown and sent to India.

### 3.4. Surface Behavior of Copper Single Crystals in Fused Sodium Chloride

J. Kruger, Metal Reactions Section and

K. H. Stern, Electrochemistry Section

This work is an extension of the study described under Section 5.24 of NBS Technical Note 174. The same approach and techniques are being applied to the study of copper. This work which is in its preliminary stages has thus far revealed that the crystallographic orientation of the copper substrate has no influence on the rate of etching at 900°C in the presence of air.

### 3.5. The Effect of Point Defects on the Dynamic Properties of Crystals

J. B. Wachtman, Jr. and Sam Spinner,

Physical Properties Section

Elastic and electrical properties are being studied as a function of temperature and frequency, and the results interpreted in terms of chemical impurities and related point defects. A program of measurements on doped magnesium oxide, MgO, and doped rutile, TiO<sub>2</sub>, is in progress. A new internal-friction peak has been discovered in nickel-doped rutile. This peak is being studied to see if illumination of the crystal during measurement reduces the peak as might be expected from results on the effect of light on the electron-spin-resonance spectrum. The present two-terminal electrical measurements will be supplemented by four-terminal measurements as soon as a new four-terminal holder is completed. Previous work on the relaxation process associated with CaO in ThO<sub>2</sub> is in press (Wachtman, 1963). The elastic constants for rutile (Wachtman, Tefft, and Lam, 1962) and for strontium titanate (Wachtman, Wheat, and Marzullo, 1963) were published. The latter paper describes a mathematical analysis which permits cubic crystals of arbitrary orientation to be used in elastic-constant determinations.

Theoretical work in collaboration with H. S. Peiser (Crystal Chemistry Section) has been continued. This work concerns the lowering of crystal symmetry by an applied stress or electric field and the classification of the point-defect relaxation processes permitted by the remaining symmetry. A survey of the effect of homogeneous stress on the symmetry of the common-oxide structures and a discussion of the internal friction permitted by symmetry is in press (Wachtman, Peiser, and Levine, 1963).

### 3.6. Precision Measurement of the Fundamental Electrical Properties of Semiconductor Crystals

J. C. French, L. J. Swartzendruber,

G. G. Harman, and H. A. Schafft,

Electron Devices Section

Experimental equipment has been set up for the preparation of accurately dimensioned semiconductor samples and for the resistivity measurements which will be made using a specially constructed traveling probe in conjunction with a potentiometric technique for the comparison of the resistance of the semiconductor with a standard resistor. A chopped current is used to minimize the effects of thermally induced voltages. In the first homogeneity measurements, rectangular parallelepiped samples will be used, with the probe system measuring the potential developed by a current flowing through the bar as a function of position of the probe with respect to a reference electrode at one end of the bar.

In preparation for these measurements, some studies are underway of the limitations imposed by the characteristics of the probing needle, the semiconductor surface, and their interaction. Specifically, measurements have been made of the relations of the needle tip radius, the force of application, and the surface finish of the sample to rectification

Figure 7. Wear of a  $40\mu$  radius tungsten carbide needle on a silicon surface lapped with  $5\mu$  abrasive. (a) and (c) show the needle before and after 75 applications with a force of 100 grams. On (b) and (d) interference fringes are superimposed to yield a quantitative measure of the needle surface.

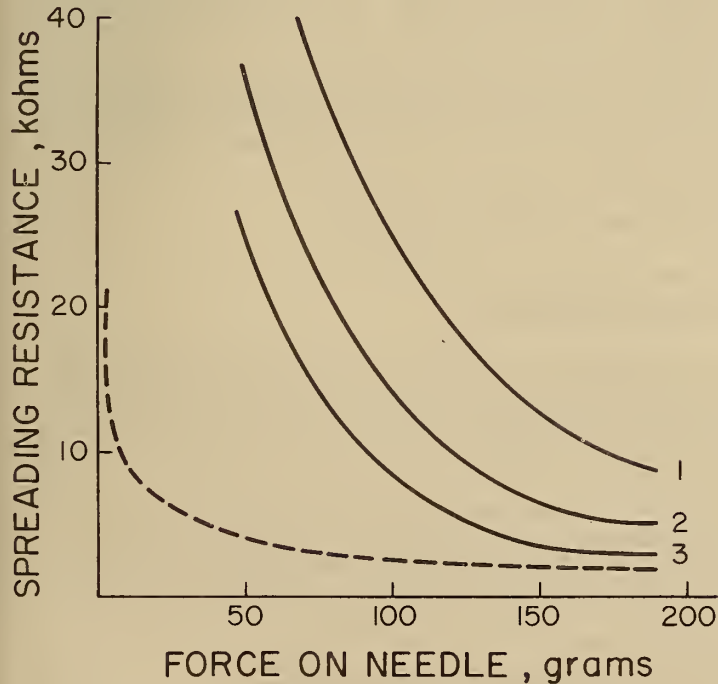
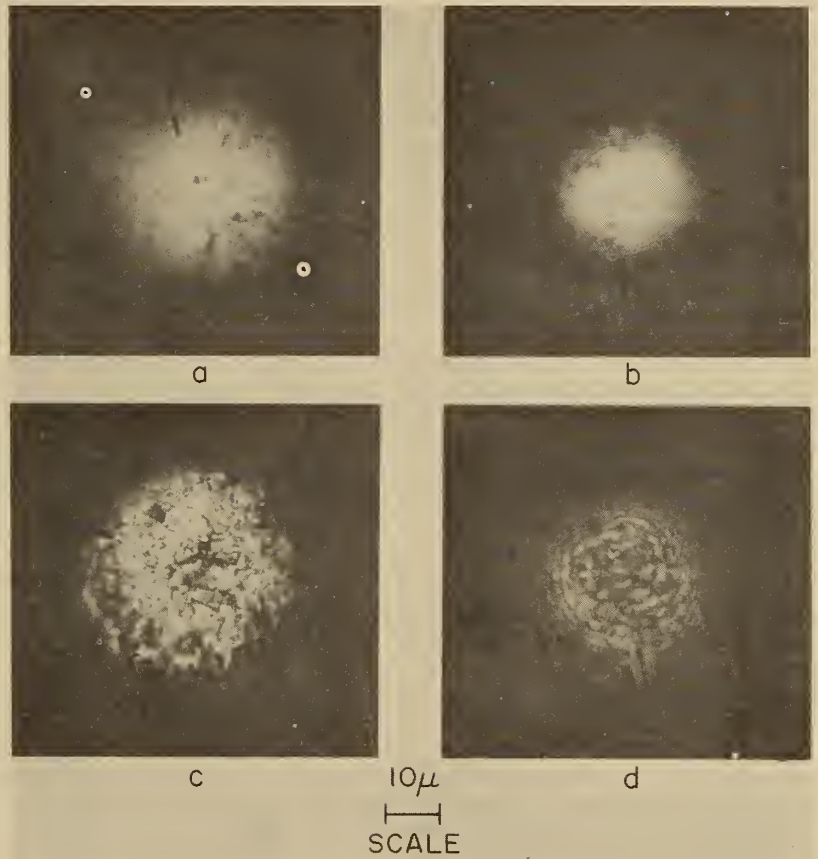


Figure 8. Typical spreading resistance vs. needle force curves as obtained with a  $40\mu$  radius tungsten carbide needle on 10 ohm-cm p-type silicon. For curve 1 the silicon was highly polished, for curve 2 the surface was lapped with a  $5\mu$  abrasive, and for curve 3 the surface was lapped with  $11\mu$  abrasive. The dotted line is a theoretical curve for perfect needle contact. Curves 1, 2 and 3 are mean curves, as some variation occurs, especially at the lower forces.

effects at the contact and to such factors as needle wear, the accuracy of sample-dimension measurement and probe location, as well as the electrical sensitivity and linear resolution of the probe system. The electrical sensitivity of the system is limited in part by the spreading resistance of the needle-semiconductor contact, and the sensitivity, in turn, provides one limit to the minimum detectable difference in voltage and hence to the linear resolution as the probe is advanced along the sample.

Figures 7 and 8 illustrate some of these effects for tungsten carbide tips applied to silicon surfaces. Along with other considerations, such data lead to the conclusion that in the resistivity range of interest (initially about 0.1 to 10 ohm-cm), practical limits of potential and linear resolution of a few microvolts and a few microns respectively are presently imposed by surface conditions.

In Section 5.14 of NBS Technical Note 174, a reference was made to the study of second breakdown in transistors (project leader, H. A. Schafft). This is a widely observed but unexplained phenomenon which limits transistor capabilities. There is reason to believe that crystal defects influence the initiation of this breakdown. Some evidence in support of this hypothesis was found in our measurements which showed that the distribution of failure sites due to second breakdown was not compatible with the way in which the theoretical current density depends on base drive. Examination of the region around these failure sites has failed to disclose the existence of defects in the crystal or in the device fabrication to account for this inconsistency. However the defect may have disappeared as a result of the local melting of the crystal at the failure site. The use of temperature-dependent phosphors has begun in order to locate the region in the transistor where second breakdown occurs. This will make possible the study of the crystal at these regions before catastrophic failure.

The electroluminescence and contact studies\* (project leader G. G. Harman) have continued with investigations of the surface barrier on silicon carbide following the methods of papers cited in the previous report (NBS Technical Note 174 Section 5.14). Work on the observation and application of charge stored in the surface states on silicon has been completed with the publication during this period of the pertinent results (Harman, Raybold, and Meyer, 1963 and Swartzendruber, 1963).

Further results on the studies of muscovite mica, which have now been completed, were recently published (Ruthberg, Barnes, and Noyce, 1963a and b)\*\*.

A new project (under J. C. French) has been established for the purpose of making available solid-state device technology as far as it may help the experimental capabilities at NBS. Facilities for crystal orientation, sawing, lapping, polishing, alloying, diffusion, and lead attachment are in preparation.

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

R. D. Deslattes,  
Crystal Chemistry Section

This project is planned to include both studies of long wavelength X-ray spectra and crystal characterization by means such as diffraction topography. Activities during the period of this report were confined to component production and assembly of the apparatus required for the above studies.

The planned spectroscopic studies require a vacuum two-crystal spectrometer and associated electronic instrumentation. The spectrometer still lacks a completed X-ray tube and detector. The setting circles are not yet available. However, the spectrometer itself has been assembled and evacuated without difficulty. Sufficient electronic equipment has been obtained to permit manual operation.

\* This work was supported in part by the Air Force Cambridge Research Center.

\*\* This work has been supported in part by the Government Services Administration.

All the major components for a Ross-mounting two-crystal instrument of considerable mechanical stability and angular sensitivity have been completed. Its full stability will be realized after the assembly has been mounted to a diabase block. Preliminary tests show an axial stability of better than one second for the second crystal mount and a maximum error of one second for the first crystal slide. The tangent drive is read by a ten-part vernier to 0.1 second. The electronics required for manual operation of this instrument have been obtained. During the next six months it is planned that both systems will be in routine operation. The provisions for automatic data recording will then be implemented and absolute-angle measuring facilities installed.

### 3.8. Spectroscopy Applied to Crystal Growth

G. L. Pollack, Crystal Growth Section

The effect of impurities on crystal growth is being studied by examination of absorption spectra of typical diatomic "impurities" in solid solution with rare gases. From these experiments such processes as zone refining of crystals and transport in crystals may be studied (Pollack, 1964). In addition, results of interest for molecular spectroscopy have been found from these studies (Pollack and Broida, 1963b).

### 3.9. Improved Sources for Spectrographic Analysis

B. F. Scribner, M. Margoshes, and S. D. Rasberry,  
Spectrochemistry Section

a. Gas-stabilized arc: The gas-stabilized arc (Margoshes and Scribner, 1963) was developed to improve the precision of spectrographic analyses. A study of the detection sensitivity of this source for several elements in dilute aqueous solution and in various matrices is presently in progress. In addition, inter-element effects on emission intensities as well as the precision of analysis for major and minor constituents using this source will be studied.

b. Gas-sheathed arc: A device has been designed and built which provides a controlled atmosphere of any desired composition while retaining the speed of analysis that characterizes emission spectroscopy. By enclosing the electrodes and the discharge in a concentric tube of flowing gas, many of the practical difficulties of previous designs have been eliminated. A systematic study is now in progress on the effect of controlled atmospheres on the vaporization and excitation in arc discharges, particularly in terms of the effect on the sensitivity of detection of the impurities in highly purified materials.

### 3.10. A Laser Microprobe for Analysis of Very Small Samples

B. F. Scribner, M. Margoshes, and S. D. Rasberry,  
Spectrochemistry Section

The laser microprobe mentioned in NBS Technical Note 174 Section 5.9 was delivered by the manufacturer in May. Figure 9 shows an over-all view of the device. Since this represents the first such instrument delivered by the manufacturer, considerable investigation will be needed before the device can be applied to routine analyses. Studies are in progress to determine the best operating conditions for the instrument, to optimize the illumination of the spectrograph and to establish methods for quantitative analysis.

The instrument uses a ruby laser which produces a pulse having a duration of  $10^{-7}$  second and a peak power of  $10^6$  watts. A metallurgical microscope is used to select the portion of the sample to be analyzed and to focus the laser beam on this spot. The pulse will vaporize any solid material and at optimum focus it will form a crater 50 microns in diameter and 25 microns deep (total volume  $\sim 3 \times 10^{-8}$ ). The spot can be made wider and shallower by defocusing the laser beam. The microprobe should allow the analysis of very small samples such as portions of a specific crystal face or of segregates or inclusions in samples.



Figure 9. The Laser Microprobe.

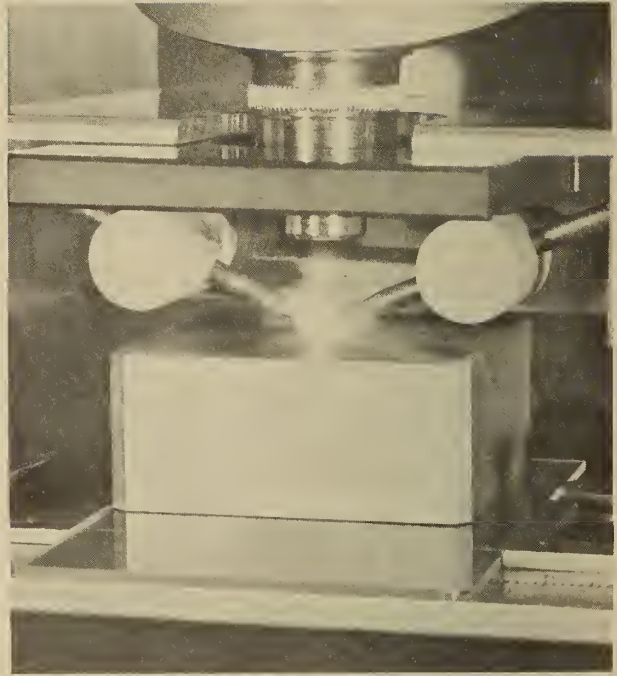


Figure 10. View of the sample and electrodes at the moment of vaporization and excitation. The eyepiece of the metallurgical microscope is just above the electrodes.

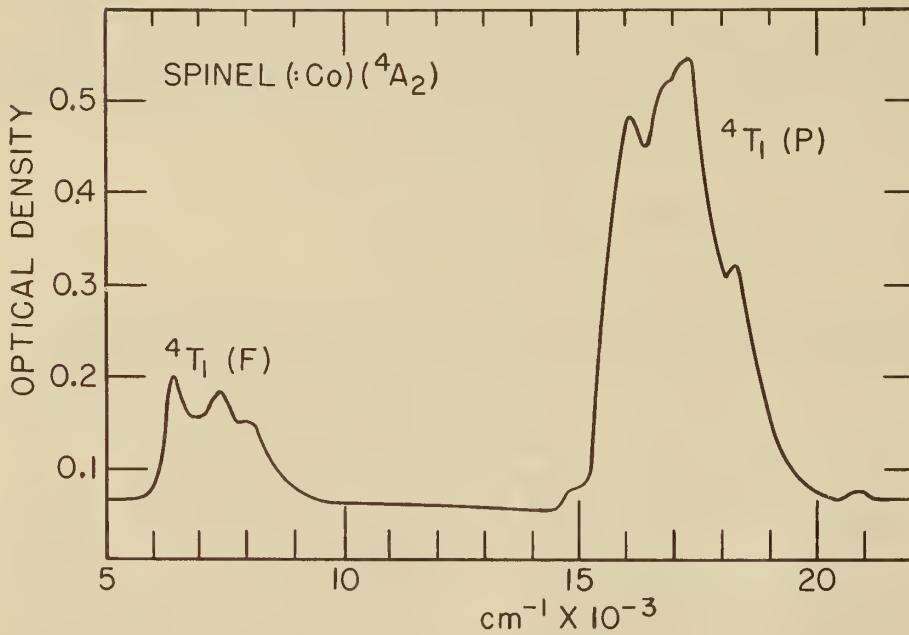


Figure 11. Spectrum for Mg-Al spinel with small concentration of Co.



The spectra of the elements in the vaporized sample are excited by a variable spark discharge between two graphite electrodes and are analyzed spectrographically. Figure 10 shows the sample and electrodes at the moment of vaporization and excitation.

### 3.11. Optical-Property Studies

R. W. Dickson,

Physical Properties Section

A low-temperature holder for a ruby laser crystal is being constructed. It is intended to control the frequency of the laser beam by controlling the temperature of the laser crystal. The resulting beam will be used in the study of clustering of chromium ions in ruby.

### 3.12. Optical Properties of "Pure" and Impure Crystals

L. H. Grabner and R. F. Blunt,

Solid State Physics Section

#### a) Semiconductors\*

The optical equipment is now in the stage that measurements of photoconductivity can be made under simultaneous excitation by two sources. Good quality CdTe samples (see Section 2.2) are presently being investigated.

#### b) Defect Studies

Spectra of cobalt-doped spinel have been recorded at room temperature, 78°K, and 4°K (see Fig. 11). There is strong indication that the  $\text{Co}^{++}$  ion is situated in a tetrahedral site. The major bands at  $\sim 7,200 \text{ cm}^{-1}$  and  $\sim 17,000 \text{ cm}^{-1}$  are identified as the  ${}^4\text{A}_2(\text{F}) \longrightarrow {}^4\text{T}_1(\text{F})$  and the  ${}^4\text{A}_2(\text{F}) \longrightarrow {}^4\text{T}_1(\text{P})$  transitions, respectively. The D value is  $\sim 400 \text{ cm}^{-1}$ . Yet to be explained are the structure of these bands and the absence of the  ${}^4\text{A}_2(\text{F}) \longrightarrow {}^4\text{T}_2(\text{F})$  transitions (expected at about  $3,500 \text{ cm}^{-1}$ ). It is possible that the latter is masked by the presence of an OH-band (which has been observed both in clear and in Co-doped spinel).

### 3.13. Automation of Single-Crystal X-Ray Diffraction Intensity Measurements

F. A. Mauer,

Crystallography Section

In the past, X-ray diffraction patterns used in the determination of crystal structure were almost always recorded on photographic film. Considerably more accurate data can be obtained by direct measurement of the diffracted-beam intensity using a proportional or scintillation counter. With the enhanced speed and precision of measurement the intensity data may be useful as a measure of crystal perfection as well as in structure analysis.

Direct measurement of intensities requires orientation of the crystal with respect to three axes, and the counter with respect to a fourth for each of a thousand or more reflections. For each reflection a fairly elaborate procedure is followed in measuring the integrated intensity. When carried out by hand, the method is slow, requiring the constant attention of a skilled operator for periods of six weeks or more.

Several laboratories, particularly in England, have adopted automatic equipment for setting the crystal and recording the integrated intensities. At the National Bureau of Standards a study of existing automatic single-crystal diffractometers has been completed

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\* This work was supported by the Office of Naval Research.



Figure 12. Laue diagram of a  $\sim 3$ -mm thick ammonium dihydrogen phosphate crystal section perpendicular to the fourfold axis



Figure 13. Laue diagram of potassium crystal showing much orientation spread.



Figure 14. Enlarged Laue diagram of 2-cm thick aluminum crystal grown by Bridgman technique.



Figure 15. Two half Laue diagrams of ammonium dihydrogen phosphate crystals grown respectively top with and bottom without addition of  $\text{Cr}^{3+}$  ions. Corresponding Laue spots are diagonally opposite each other.

and specifications for an improved instrument have been drawn up. At least two manufacturers are prepared to build such an instrument, and it is expected that one will be ordered in the fall of 1963. In the meantime, measurements are being carried out by hand to determine the exact procedures the machine will be programmed to execute.

### 3.14. High-Voltage Laue Photographic

#### Inspection of Large Single Crystals

B. Paretzkin and H. S. Peiser,  
Crystal Chemistry Section

The high-voltage method has been further developed (compare NBS Technical Note 174 Section 5.13). X-ray diffraction photographs have been taken of single crystals through walls of vessels and furnaces composed of polycrystalline materials.

Figure 12 shows a Laue diffraction picture of a good ammonium dihydrogen phosphate crystal. Figure 13 illustrates a bad potassium crystal. Figure 14 shows enlarged diffraction spots of an aluminum crystal grown by a Bridgman technique. The topographic detail demonstrates the presence of polygonization absent from strain-annealed crystals.

Primary extinction is a feature of Laue photographs of good solution-grown crystals of ammonium dihydrogen phosphate. The addition of impurity chromium ions to the growth bath reduces the attenuation of strong diffraction spots due to primary extinction (Figure 15).

### 3.15. Dilatometric Studies of Polymers

J. Powers and F. A. Quinn,  
Macromolecules Synthesis and Structure Section

The polymorphism previously reported in polybutene-1 and polypentene-1 (NBS Technical Note 174 Section 5.21) is being investigated by wide-angle X-ray diffraction.

In addition, dilatometry is being used to delineate the maximum in the isothermal crystallization rate in polystyrene. Morphological and growth-rate studies using photomicrographic techniques are being carried out concurrently. Preliminary specific-volume/temperature measurements show a change in slope at about 95°C indicating that the isotactic polymer has a glass transition temperature in the same range (80°-100°C) as the atactic.

## 4. Crystal Physical Properties

Contributions to this section are concerned with the physical properties of crystals which do not depend primarily upon the degree of crystal perfection or whose dependence on that perfection is not the principal aim of the investigation.

### 4.1. Velocity of Sound in Ice Single Crystals<sup>\*</sup>

T. M. Proctor, Sound Section

Thermal expansion and specific heat data [Butkovich, J. Appl. Phys. 30, 350 (1959) and Flubacker, Leadbetter, and Morrison, J. Chem. Phys. 33, 1751 (1960)] have indicated that single crystals of regular ice show an unusual phonon spectrum at low temperature. Elastic constants for ice found in the range of 0°C to -30°C indicate a large discrepancy between  $C_V$  as measured at low temperatures (20°K) and  $C_V$  as calculated from these constants. An attempt to correlate velocity of sound data with specific-heat data at low temperatures has been undertaken in a project started about 1-1/2 years ago. The primary aim of this project is to measure the velocity of sound in single crystals of ice down to liquid-helium

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

temperatures.

Techniques for measuring velocity of sound in solids down to liquid-helium temperatures have been investigated. A method which measures the velocity with a high precision has been devised and the apparatus is almost complete (a low temperature cryostat has been in use for almost a year; velocity measurements have been made down to 55°K a number of times). Techniques for growing large single crystals of ice have been refined. (Samples of 1-1/2 inches in diameter and 2 inches long have been grown.) Crude early measurements down to liquid-nitrogen temperatures indicate that ice has a positive slope in its velocity temperature curve. These data do not show the presence of the expected low-temperature vibrational mode. It may well be that liquid-nitrogen temperatures are just not low enough to detect this mode but it may be detected when the experiment is performed at liquid-helium temperatures.

#### 4.2. Electronic Transport<sup>\*</sup>

H. P. R. Frederikse and J. H. Becker,  
Solid State Physics Section

Measurements of conductivity  $\sigma$ , Hall effect  $R_H$  and thermoelectric power  $\alpha$  are aimed at a better understanding of the electronic transport and the defect structure of oxides [in particular  $TiO_2$  and  $SrTiO_3$ , (also  $Fe_2O_3$  and  $Cu_2O$ ) compare Becker and Hosler (1963) and Yahia (1963)]

Determination of  $\sigma$  and  $R_H$  at helium temperature show a temperature dependence which indicates conduction in impurity levels (or bands). Excitations to higher bands are studied by measuring the conductivity and Hall coefficient under illumination. The increase of  $R_H$  is strongly dependent on the light intensity. Presently the wavelength dependence of these photo effects is being examined.

Investigations of the anisotropy of the Hall effect and the Seebeck coefficient over the entire temperature range seem to confirm the existence of a "second" conduction band within 0.05 - 0.10 eV of the bottom of the "first" conduction band.

Measurements of the Seebeck coefficient  $\alpha$  of  $TiO_2$  and of  $SrTiO_3$  down to 15°K have shown that the phonon-drag effect accounts for most of the magnitude of the coefficient of rutile at low temperatures, while it seems to be absent in  $SrTiO_3$ .

#### 4.3. Hall-Effect Measurements<sup>\*\*</sup>

S. Rubin, Engineering Electronics Section

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

A proposed Standard for Hall-generator definitions, terminology, letter and graphic symbols is in process of preparation. There is included a definition of linearity error as a percentage of reading, in addition to the usual linearity error as a percentage of full scale. Descriptions of measuring methods are included as an appendix to the definitions. The proposed Standard has been submitted to the American National Committee of the International Electrotechnical Commission, TC 47, which, through its affiliation with the International Organization for Standardization, acts in a consultative capacity to UNESCO.

Additional work in the development of instrumentation for the precise measurement of small magnetic fields in restricted areas using electron-paramagnetic resonance is proceeding.

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\* This work was supported in part by the Office of Naval Research

\*\* This work was supported by the Bureau of Naval Weapons.

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

J. H. Wasilik,

Solid State Physics Section

The dielectric constant  $\epsilon'$  of monocrystalline lead fluoride,  $\text{PbF}_2$ , has been measured at room temperature and at frequencies from  $10^5$  to  $10^7$  cps. At  $300^\circ\text{K}$  the value of  $\epsilon'$  appears to be  $28.7 \pm 1.4$ ; preliminary results indicate a small increase at helium temperatures. The refractive index of  $\text{PbF}_2$  has been measured; this additional information permits the determination and analysis of the polarizabilities of the two ions.

Attempts to observe the loss due to excitons are continued; the substance under investigation is now  $\text{CdS}$  rather than  $\text{Cu}_2\text{O}$ . The lifetime of excitons in the former is considerably longer than in the latter, producing larger exciton concentration in  $\text{CdS}$ .

#### 4.5. Electron-Lattice Interaction

R. P. Hudson, Heat Division

In both low-frequency and high-frequency phases of the work, efforts of three part-time staff members have been concentrated on instrumentation.

##### a) Audiofrequency Measurements

The new mutual-inductance bridge, one of three constructed recently in the Cryogenic Physics Section, was set up. A simplified selective amplifier was constructed to replace the one taken over from the magnetic-cooling apparatus. An electronic thermostat for the helium bath was constructed in collaboration with the Instrumentation Division.

##### b) Pulsed Microwave Measurements

A plastic X-band microwave cavity was manufactured but to date has not been silvered satisfactorily; even so, a  $Q$  of 4000 was achieved so that the prospects are good for the eventual production of a very good cavity. Also designed and constructed were a separate filament-power supply to reduce the klystron-noise level; a small d.c. supply for applying bias to the diodes in the microwave switch; a simple solid-state phase-sensitive detector for conventional presentation of e.p.r. signals during check-out procedures.

A superheterodyne unit (radar receiver) was borrowed from the Instrumentation Division and put into operating condition; it is not, however, an ideal unit for the present application and is currently being replaced by a radar receiver obtained commercially; a power supply for it is under construction. [The need for high-sensitivity and wide-band detection seems to dictate use of the superheterodyne method although the video-detection method may prove adequate in some instances.]

The vertical-axis-rotation bearing originally supplied with the new electromagnet was unsatisfactory; it has just been replaced with a heavy-duty bearing, which works well.

#### 4.6. Studies in Solid-State Theory

A. H. Kahn, Solid State Physics Section

a) The tight-binding calculation of the electronic energy bands of rutile,  $\text{TiO}_2$ , has progressed to the stage where the only remaining work is the computer programming. This is in progress. Results will be compared with experimental data on galvanomagnetic and optical properties of rutile crystals.

b) Calculations similar to those on  $\text{TiO}_2$  are now being performed for  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  in an attempt to understand similarities and differences in the electrical and optical behavior of these related compounds (see Section 4.2).

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This work was supported by the Atomic Energy Commission.

c) A study of transport effects in tetragonal semiconductors has been carried out by W. C. Hernandez, Jr. and A. H. Kahn (1963). The effect of energy-band anisotropy on the galvanomagnetic and thermoelectric coefficients has been determined for simple ellipsoidal models.

#### 4.7. Isotopic Impurities and Energy Transport in Harmonic Crystals

R. J. Rubin,

Temperature Physics Section

Energy transport in harmonic crystals containing isotopic defects is being investigated. A general theoretical model has been studied in which a harmonic crystal is divided initially into two regions characterized by different temperatures. Cooling curves have been calculated for several one-dimensional crystals: 1) an infinite perfect crystal; 2) an infinite crystal containing one isotopic defect; and 3) several 100- and 200-particle isotopically disordered crystals consisting of equal numbers of two isotopes. An account of this work will appear in the August 1 issue of the Physical Review. (See also Rubin, 1963).

At present the phonon-transmission characteristics of a slab of isotopically disordered crystal inserted in a perfect crystal are being studied.

#### 4.8. Cryomagnetic Theory

J. C. Eisenstein,

Cryogenics Section

During the past year work was concentrated on magnetic and optical properties of rare-earth trichlorides. These compounds are interesting because of the possibility that they may become ferromagnetic at very low temperatures. Detailed analyses were made of the optical spectra of  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  in solid  $\text{LaCl}_3$  and two papers were written on these ions. In a third paper the spectra of  $\text{Nd}^{3+}$  in  $\text{LaCl}_3$  and  $\text{Nd}^{3+}$  in  $\text{LaBr}_3$  were analyzed and compared and it was shown how the host lattice affects the energy levels. A fourth short paper dealt with the magnetic properties of the ground state of  $\text{Ce}^{3+}$  in  $\text{LaCl}_3$ . Finally, the angular parts of the wave functions for three equivalent f electrons which are eigenfunctions of  $L^2$ ,  $S^2$ ,  $J^2$  and  $J_z$  were tabulated.

#### 4.9. Energy Transfer Below 1°K

J. F. Schooley and E. R. Pfeiffer,

Cryogenics Section

This project has the responsibility for the preparation of single crystals used in research in several of the projects in the Cryogenic Physics Section in addition to the measurement of energy transfer at low temperatures.

Hydrated crystals, principally ethylsulfates and double nitrates of the rare earths are grown by the techniques of isothermal evaporation of solutions, of temperature reduction of saturated solutions, and of thermal gradient pumping within solutions.

Experiments on the thermal conductivity of single crystals of the above type at approximately .02-.10°K by means of the steady-state temperature gradient technique are in progress. The secondary thermometers employed in this technique are the paramagnetic susceptibility of the crystal and the anisotropy of gamma radiation from oriented radio-nuclei.

Two papers describing preliminary work have recently been published (Schooley, Hoppes, and Hirschfeld, 1962, and Schooley and Hoppes, 1962).

#### 4.10. Low-Temperature Nuclear Orientation

E. Ambler, H. Marshak, R. S. Kaeser, and R. B. Dove,  
Cryogenics Section

Helium-3 refrigeration has been used to produce a substantial degree of nuclear alignment in single crystals of holmium ethylsulfate, and bremsstrahlung from the NBS betatron has been used to study the  $(\gamma, n)$  cross-section as a function of angle between the beam and the crystalline alignment axis. The anisotropy found demonstrates the tensor nature of the nuclear polarizability of holmium.

#### 4.11. Low-Temperature Thermometry

H. Plumb, G. Cataland, and M. Edlow,  
Cryogenics Section

A portion of the NBS effort in low-temperature thermometry is concerned with the resistance of impurity-doped germanium crystals as a sensitive function of temperature below 20°K. In similar work with carbon resistors, the resistance was found to obey the following semi-empirical equation between 2° and 20°K:

$$\log R + K/\log R = A + B/K$$

Here, A, B, and K are treated as constants to be determined experimentally.

#### 4.12. Nuclear-Resonance Thermometry

S. F. J. Read,  
Temperature Physics Section

The purpose of the project is to measure the temperature dependence of pure quadrupole and nuclear-resonance frequencies; and to investigate the applicability to precision thermometry.

The quadrupole-resonance frequency of  $\text{Cl}^{35}$  in  $\text{KClO}_3$  is one possible thermometer. The frequency is believed to depend on both impurities and crystal imperfections.  $\text{KClO}_3$  crystals are being grown and the reproducibility of the thermometer is being investigated.

#### 4.13. Metal-Oxide Melting-Point Standards

S. J. Schneider,  
Crystallography Section

The program, which was initiated in mid 1962, consists of three distinct areas:  
(1) compilation of melting-point data through a critical review of world literature;  
(2) experimental determination of the melting points of many oxides under various environmental conditions and the selection of several oxides deemed suitable for use as standards;  
(3) refinement of the melting points of the selected oxides.

During the past months, phase(1) has been completed and will be published (Schneider, 1963). The compilation indicated that no single metal oxide has been studied in sufficient detail to justify its use as a melting-point standard. Equipment for phase(2) has been assembled and is currently being tested.

#### 4.14. Reduction of Space Groups to Subgroups by Homogeneous Strain

H. S. Peiser, Crystal Chemistry Section; and

J. B. Wachtman, Jr., and R. W. Dickson,  
Physical Properties Section

Tables showing the lowering of space-group symmetry for all space groups and all types of homogeneous strain has been accepted for publication (Peiser, Wachtman, and Dickson, 1963).

The symmetry of strained crystals is important in the following considerations:

(1) The presence or absence of internal friction resulting from the motion of point defects in a crystal can depend upon whether or not the initially equivalent sites accessible to the defect are inequivalent in the strained crystal. (2) Any tensor property of a crystal, such as piezoelectricity, depends primarily upon the symmetry of the unstrained crystal, but additional tensor components may be introduced by straining the crystal in such a way as to change its symmetry. (3) A classification of the types of polymorphism of crystals has been proposed by M. J. Buerger; in some categories no bonds are broken but only a symmetry change takes place. Some structural changes can be induced by homogeneous strain. (4) Solid solution of an impurity atom is usually accompanied by strain which may lower the symmetry. (5) Large strain fields exist near dislocations and accompanying symmetry changes may be associated with large local variations in physical properties such as enhanced diffusion near a dislocation. (6) Strain-induced alteration of symmetry may cause change in electron-spin resonance or infrared absorption; measurements of these changes may give information on the type of site occupied by a given point defect.

#### 4.15. Magnetic-Susceptibility Measurements

B. W. Mangum, Cryogenics Section

Various anhydrous paramagnetic crystals, principally rare-earth trihalides, have been grown in a temperature gradient furnace.

A mutual-inductance coil, a mutual-inductance bridge, and the cryostat have been completed, and measurements of paramagnetic susceptibilities in the range 1°K-300°K are contemplated.

#### 4.16. Magnetic-Resonance Studies I<sup>\*</sup>

T. Chang, R. A. Forman, and R. E. Payne,  
Solid State Physics Section

##### a) Electron-Spin Resonance

The study of Mo-doped rutile,  $TiO_2$ , was brought to a successful conclusion. The spectrum is shown in figure 16. The use of a cavity designed for circularly polarized microwave radiation enabled the unambiguous determination of the sign of the g-factor. An account of this work is being written (T. Chang, 1963).

Other studies are concerned with the  $Ti^{3+}$  center in reduced  $TiO_2$ . Preliminary measurements confirm the results of P. F. Chester [J. Appl. Phys. Suppl. to 32, 2233 (1961)].

##### b) Nuclear-Magnetic Resonance and Quadrupole Resonance

The study of the N-nucleus in azides is being continued. The quadrupole coupling constants of each of the three N nuclei in (gaseous)  $HN_3$  were determined from the microwave spectrum. The assignment was made possible by using three  $N^{15}$ -substituted species

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\* Supported in part by ERDL-Ft. Belvoir, Department of the Army.



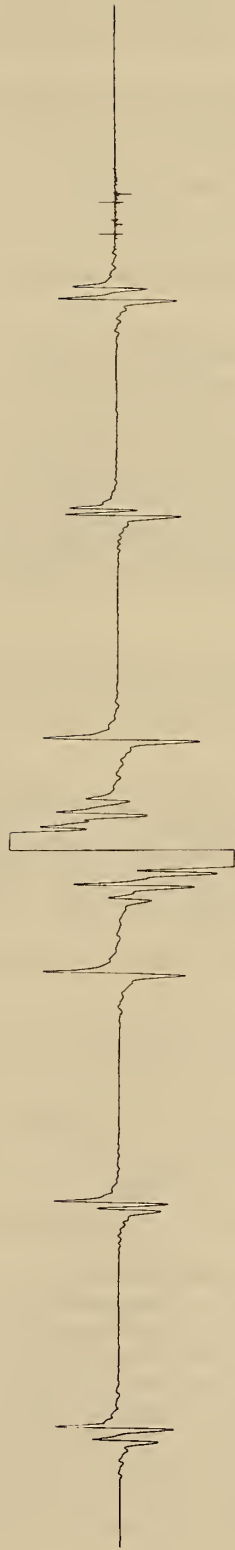


Figure 16. Electron spin resonance spectrum of  $\text{Mo}^{5+}$  in rutile ( $\text{TiO}_2$ ) -- frequency, 9 kMc; temperature,  $78^\circ\text{K}$ .

(Forman and Lide, 1963).

The chemical shifts of  $N^{14}$  in sodium azide solution have been measured. The determination was made relative to a saturated solution of sodium nitrate. No effect of solution concentration was noted on the chemical shifts (Forman, 1963).

Investigations of nuclear resonances in the internal field of antiferromagnetic materials are being planned. Oscillators are tested in the 30-80 Mc range.

#### 4.17. Magnetic-Resonance Studies II

L. M. Matarrese, J. S. Wells, and A. R. Cook,  
Radio and Microwave Materials Section

In connection with the EPR investigation of amethyst the EPR spectrum of iron-doped synthetic quartz is being studied at X-band and K-band. This spectrum has the same general features as that of amethyst, but differs greatly in detail. The color of the specimens varies from pure green through green-yellow to yellow, the green being obtained under oxidizing conditions. The color makes little difference in the EPR spectra however, which, at room temperature, all resemble that of ferric ion. The spectrum consists of three sets of lines, presumably from three inequivalent substitutional sites. Each set consists of five or more fairly intense, narrow lines and many weaker ones, spread over an extremely wide field range (0-900 G at X-band). The intensities of some of the lines vary markedly with angle. There is a broad intense resonance at  $g = 2$  at X-band but not at K-band.

Crystal-field theory has been applied to the interpretation of the spectrum with rather poor results. The spin-Hamiltonian parameter  $D$  is of the order of 1000 G. We are now concentrating on the K-band spectrum in the hope of obtaining a better theoretical interpretation.

A new method of preparing X-band and K-band cylindrical cavities for EPR work has been developed. The method is described in a paper to be submitted to Review of Scientific Instruments. The cavities are molded from epoxy resin and have a thin silver wall with a spiral groove running from top to bottom. Besides suppressing unwanted modes, the spiral groove permits excellent penetration of 100 kc magnetic field modulation.

A marginal oscillator operating in the 30-60 Mc range has been built for use in the ENDOR experiments which are planned.

Millimeter-wave components are being acquired for the planned investigation of anti-ferromagnetic resonance.

#### 4.18. Microwave Measurements on Single-Crystal Ferrimagnetics

A. S. Risley,  
Radio and Microwave Materials Section

Measurements have been made of the ferrimagnetic resonance of single crystals of manganese ferrite and nickel-zinc ferrite. The data were obtained on rods and spheres of these materials at a frequency of 9.15 Gc. The results of the linewidth,  $H$ , measurements were: Ni-Zn;  $H_{rod} \approx H_{sphere} \approx 900$  oersteds.  $M_n; \Delta H_{rod} \approx 22$  oersteds with  $H_{sphere}$  ranging from 26 to 40 oersteds as a function of its orientation with respect to the D.C. field. The sphere measurements were performed on a sample whose average surface roughness was 63 microns. The same sphere, polished to 0.2 microns, varied between 20 and 25 oersteds with orientation. These tests were made without reference to X-ray orientation studies. The stock from which the samples were fabricated was supplied to the National Bureau of Standards in May of 1953. Further work is planned using X-ray orientation observations, provided other suitable crystals are obtained.

#### 4.19. Work Functions of Perfect Single-Crystal Planes of Tungsten

R. D. Young, Electron Physics Section

Recent developments in field-ion microscopy have enabled the creation and observation of atomically perfect single-crystal planes of refractory materials. Field electron emission from tungsten single-crystal planes is being employed to measure the work function of these well characterized surfaces. The present experiments also include provision for simultaneous measurement of the energy distribution of photoelectric emission and field electron emission from the same plane, permitting an absolute measurement of the work function of these perfect planes. Since all low-index planes are simultaneously available, it will be possible to study the dependence of work function on the detailed atomic arrangement of a particular crystallographic plane.

#### 4.20. Interaction of Low-Energy Particles with Surface Atoms

R. D. Young and R. S. Will, Electron Physics Section

A technique has been developed for studying interactions in the few milli-electron-volt range between uncharged particles and surface atoms. In this work the field-ion microscope is employed in the desorption phase to carry out such interactions, and in the best image phase to determine which atoms have interacted. In this way the effect of crystal plane (number of nearest neighbors, etc.) on the interaction process can be studied. Future work will include the interaction of ultraviolet light with a tungsten or platinum single-crystal surface.

#### 4.21. Molecular Energy Levels

A. M. Bass, Heat Division

A study of the ultraviolet absorption spectrum of  $O_2$  in liquid and in solid argon and nitrogen has been made. As contrasted with the spectrum of gaseous  $O_2$ , the Schumann-Runge bands (1750 to 2000 Å) show a slight shading to the violet and a displacement to frequencies which are lower by 50 to 400  $cm^{-1}$ . Little difference was noted between liquid and solid or between nitrogen and argon media.

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

D. E. Mann, Molecular Spectroscopy Section

The investigation of environmental influences on the rotation-vibration spectra of simple molecules isolated in solid rare-gas lattices has advanced along several new lines as a result of recent observations. Earlier studies of the hydrogen and deuterium halides showed the presence of both rotating and non-rotating species in various matrices. It was found that the absorption bands of the non-rotating molecules were remarkably narrow. An attempt is being made to determine precisely the actual limiting line widths, and to derive from these data an indication of the degree of coupling of the molecular motion to the lattice. In other recent studies it has been found that under certain conditions structure which appears to be characteristic of vibration-rotation band envelopes is retained in lattices even at 4°K. Several newly discovered examples are being studied to ascertain to what extent the observed envelopes reflect lattice influences on the rotational motions of the molecules. New data have recently been obtained in support of the view that water molecules trapped in solid rare-gas lattices execute nearly free rotation. Moreover, it has been found that ortho-para spin conversion is strongly induced by the presence of trace quantities of molecular oxygen in the lattice.

## 5. Crystal Chemistry

Contributions to this section are concerned with studies of individual crystal phases involving crystal structure, transformations, or chemical properties not sensitively dependent upon crystal perfection.

### 5.1. Phase Equilibria

R. S. Roth and E. M. Levin,  
Crystallography Section

Research is being conducted on glass-forming systems containing  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$  or  $\text{GeO}_2$ ; on systems of interest in electronic research such as those containing  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$  or  $\text{V}_2\text{O}_5$ ; and on very refractory oxides, such as the rare-earth oxides.

A paper elucidating the complex, stable and metastable, polymorphic relations of  $\text{Bi}_2\text{O}_3$  has just been prepared for publication. This paper should enable scientists in research and industrial laboratories to obtain a better understanding of this oxide widely used as an additive in the glass and electronic industries. Another contribution has been the discovery that the solid solution widely reported to occur with additions of small cations to  $\text{Nb}_2\text{O}_5$  actually represents discrete phases with definite  $\text{Nb}^{5+}$ -to-cation ratios. The complete elucidation of the composition and structure of these phases should prove of value in the fields of electronic ceramics and metal-oxidation studies.

Present plans call for a study of the discrete phases of  $\text{Nb}_2\text{O}_5$  systems and a complete study of rare-earth oxide/boric oxide systems.

For related work see Roth, Waring, and Levin (1963) and Schneider and Waring (1963).

### 5.2. Crystal-Structure Analysis

S. Block, H. M. Ondik, and A. Perloff,  
Crystallography Section

The program of crystal-structure analysis has several facets: (a) evaluation of methods of structure analysis, (b) determination of structural principles of inorganic compounds such as borates and phosphates and (c) compilation of single-crystal data. In the past few months papers have been submitted for publication which indicate the applicability and some limitations of various formulae for structure analysis, and present the crystal structure of 1-ethyldecaborane (Perloff, 1963/4),  $\text{LiK}_2\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$  (Eanes and Ondik, 1962),  $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  (Block and Perloff, 1963/4),  $\text{NaP}_3\text{O}_9$  and  $\text{Na}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$ . Arrangements are being made for publication of future volumes of the book "Crystal Data" by NBS. Work is continuing in all the above fields.

### 5.3. Standard X-Ray Diffraction Powder Patterns\*

H. E. Swanson, Crystallography Section

Patterns of pure and well characterized inorganic solids are being produced for comparison standards used in identifying crystalline materials of unknown composition. These patterns have been published in twelve volumes the most recent of which (Swanson et al., 1963) includes patterns for 37 substances, 26 of which were not previously included in the file (XRPDF) issued by the Joint Committee for Chemical Analysis by X-Ray Diffraction. The remaining eleven replace earlier and less accurate patterns taken from various sources. In all, NBS has contributed approximately 600 patterns. The need for additional patterns is expected to continue indefinitely.

\*

This work is partially supported by the Joint Committee for Chemical Analysis by X-Ray Diffraction.

#### 5.4. Rapid X-Ray Diffraction Photography of Polycrystalline Materials

R. E. LaVilla, Crystal Chemistry Section

In order to study the atomic rearrangements during transient phenomena, techniques for the rapid recording of X-ray powder diffraction patterns are being developed. These techniques will take advantage of the geometry of a fine-focus X-ray tube by coupling it to a miniature X-ray focusing camera. The applicability of a commercially available electronic image intensifier will also be explored. The desired X-ray diffraction pattern will be obtained by synchronizing the driving force causing the atomic rearrangements in the specimen with the pulsing of the X-ray tube and the grating of the image intensifier. We hope to decrease the X-ray exposure times to about a millisecond. Shorter X-ray exposures will depend mainly on increasing the X-ray tube currents. It may be possible to increase the X-ray tube current by an appreciable factor if one grossly overloads the tube causing burnout of the filament and target.

#### 5.5. Application of Borrmann Crystals to the Construction of a High-Resolution Small-Angle X-Ray Camera

H. Brumberger, Crystal Chemistry Section

The wave-length focusing property [see, for instance, Beeman, W. W., Kaesberg, P., Anderegg, J.W. and Webb, M. B., *Handbuch der Physik*, 32, 428 (1957)] of nearly perfect (Borrmann) germanium crystals cut to reflect from the  $\{220\}$  planes in the Laue position is used to obtain 1:1 image of the focal spot of a microfocus X-ray tube at a distance of 50 cm. from the crystal. Because of the perfection of the crystal, a very good image is hoped for.

For a  $100\mu$  focal spot, a diffracting sample located just past the Borrmann crystal, and a beamstop about  $200\mu$  wide, an angular resolution of  $2 \times 10^{-4}$  radians should then be attainable in the low-angle pattern.

#### 5.6. Lattice Parameters and Energies of High-Pressure Polymorphs of Some Alkali Halides

G. J. Piermarini and C. E. Weir,  
Crystallography Section

Lattice parameters of high-pressure forms of all the rubidium halides (Piermarini and Weir, 1962a) and potassium halides in addition to cesium fluoride are being determined using a high-pressure X-ray diffraction camera (Piermarini and Weir, 1962b). The alkali halides being studied have the NaCl-type structure at one atmosphere and  $25^{\circ}\text{C}$ . From present results it appears that the observed high-pressure form of all these salts has the CsCl-type structure. The measured values of the lattice parameters are being used to compare the lattice energies of the two phases in equilibrium at the transition pressure. Within experimental error it appears that the Born-Meyer theory adequately accounts for the lattice energy of the high-pressure phase.

#### 5.7. Infrared Spectroscopy of Crystalline Inorganic Borates

C. E. Weir, R. A. Schroeder, and E. R. Lippincott,  
Crystallography Section

Following on previous similar studies (Schroeder, Weir, and Lippincott, 1962) a number of inorganic borates have been prepared for infrared spectroscopic studies and initial spectra are being obtained using the null technique at room temperature. Spectral studies will be correlated with the results of other work on the X-ray crystal structure of the borates (see Section 5.2). In particular, the question of the effect of coordination of the boron on the spectra will be studied. Spectra of single crystals of the borates will

also be studied in an attempt to correlate these studies with earlier work on libration of anions.

## 5.8. Optical Observations of Pressure-Induced Transitions in Polymers

J. Powers and F. A. Quinn,  
Macromolecules Synthesis and Structure Section

Continuing the study of pressure-induced transitions in polymers (NBS Technical Note 174 Section 4.11), light-transmission measurements have been carried out. These show an abrupt change in transmission in the pressure range where thickness and morphology change suddenly. The results are reported in a letter to be published (Van Valkenburg and Powers, 1963).

## 5.9. High-Pressure Microscopy of Crystal Transformation and Growth

A. Van Valkenburg, Crystallography Section

High-pressure optical studies have been carried out on (1) the silver and cuprous halides at pressures up to 125 kilobars (2) cadmium sulphide at pressures up to 80 kilobars and (3) the high-pressure forms of ice (ice VI and VII) at pressures up to 60 kilobars. These studies were made using a diamond high-pressure cell, monochromatic light and a polarizing microscope (compare NBS Technical Note 174 Section 4.10).

The silver halides included AgI, AgBr, and AgCl obtained from commercial sources. A new birefracting phase was observed in silver iodide at 2400 bars (Van Valkenburg, 1963). Another phase, which occurs at pressures above 100 kilobars, was reported earlier by Drickamer, who assumed that it was cubic. However, the present study indicates that it is birefringent in character. It was also noted that the polymorphic pressure phase having the NaCl structure appeared to exhibit a dark reddish color at 450  $\mu$  and 3,000 bars, which suggests a fluorescence phenomena.

The cuprous halides consisting of CuI, CuBr, and CuCl all have the sphalerite or zinc-blende type structure at ambient pressures and temperatures. Since they are structurally similar it was believed that their polymorphic forms would also show similarities. Three transitions, occurring at 4,5, and 15 kilobars, were found in CuI, and three transitions were found in CuBr, two occurring at 47 kilobars and a third at 80 kilobars. Two transitions were observed, at 42 and 55 kilobars, in CuCl with a possible third in the pressure range of 80 kilobars.

Using a gasketing technique developed for the diamond high pressure cell, water was frozen at ambient temperatures. Ice VI was obtained at pressures above 10 kilobars and ice VII above 25 kilobars. The optical characteristics of these phases were observed. It was possible to grow a single crystal of ice VI from its liquid environment covering the cell's entire field of view of about 2 mm. Ice VII appears to be isotropic and ice VI is birefringent with a hexagonal outline. There also appears to be a third metastable phase that exists between water and ice VI.

## 5.10. Purification of Polymorphic Inorganic Solids and Preparation of Crystals of a Single Polymorphic Species

A. R. Glasgow, Jr., Pure Substances Section

The purpose of this research program is to extend purification by phase transports and separations to temperatures up to 1000°C, and to develop non-reactive metal systems for carrying out such processes with inorganic fluorides in the presence of hydrofluoric acid as a solvent. Particular emphasis will be placed on establishing p, T, and solubility conditions that are necessary to obtain individually the different crystalline forms of polymorphic inorganic substances.

At present the entire program is directed towards the preparation of high-purity crystals of beryllium fluoride,  $\text{BeF}_2$ , in a single polymorphic form. In addition to the preparation of crystals of  $\text{BeF}_2$  by phase transports and separations at ordinary pressures, a process similar to the hydrothermal growth of quartz from fused silica will also be applied to  $\text{BeF}_2$  with  $\text{HF}$  as the solvent instead of water and with ammonium fluoride,  $\text{NH}_4\text{F}$ , as the flux material instead of caustic soda,  $\text{NaOH}$ .

Progress to date has involved mainly assembly of equipment for performing experiments safely in a hooded area with non-reactive metal systems under closed-system operation and under controlled temperatures. The equipment when fully operable will have wide applicability beyond the specific system under study.

#### 5.11. Crystal Chemistry of Silver Iodide<sup>\*</sup>

G. Burley, Crystallography Section

Work described in NBS Technical Note 174 Section 5.25 has been continued. The zero-point motion, the kinetics of the  $\gamma$ - $\beta$  phase transformation and the epitaxial nucleation of ice by single crystals of silver iodide have been studied.

The temperature attenuation of the powder X-ray diffraction peak-heights of cubic silver iodide was measured at  $20^\circ$ ,  $78^\circ$  and  $120^\circ\text{K}$ . From this, and the room temperature exponent obtained from single crystal data, the zero-point Debye-Waller exponent was deduced as  $0.21\text{\AA}^2$ . This corresponds to a zero-point thermal vibration of  $0.05\text{\AA}$  (R.M.S. amplitude).

The transformation of the face-centered cubic to hexagonal phase has been found to obey first-order kinetics. The energy of activation is  $10.4 \pm 1.3$  kcal/mole. Within the limits of error, this is equal to the activation energy for defects, given as  $11.2$  kcal/mole in the literature. The mechanism of this transformation is therefore probably related to the generation of lattice defects.

The observations of the nucleation of ice on hexagonal silver iodide have now been extended to large single crystals. On freshly prepared crystals the ice growth is predominantly on the  $\{100\}$  and  $\{101\}$  surfaces. After irradiation with a mercury lamp the predominant growth site is the  $\{001\}$  basal plane. This behavior is in excellent agreement with the model for the photolytic breakdown of silver iodide previously proposed (Burley, 1963a) on the basis of the observed primary extinction in X-ray diffraction patterns.

The study of silver iodide is now being concluded with a radial distribution analysis of the body-centered cubic structure at  $160^\circ\text{C}$ , which is just above its lowest stability temperature, with the intention of clarifying the mechanism of the "memory" of phase retention in a cyclical process.

The structure of hexagonal  $\text{AgI}$  has now been published (Burley, 1963b).

#### 5.12. Phase Equilibria in Dilute Polyethylene-Diluent Systems

F. Gornick, Macromolecules Synthesis and Structure Section

Although a great deal of work on the crystallization behavior of polyethylene from dilute solution has been reported, very little is known about the thermodynamic parameters of the crystallization process in various solvent systems. Work is now being carried out to study the phase diagram of polyethylene in the concentration range  $0.1\%$  to  $10\%$  in solvents having varying solubilities for polyethylene. The polyethylene used consists of fractions of various molecular weights, and the solvent is the mixed-solvent system xylene-butyl cellosolve, ranging in composition from pure xylene, a good solvent, to  $50$ - $50$  xylene-butyl cellosolve, which is a very poor solvent.

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<sup>\*</sup>This work was supported by the National Science Foundation.

### 5.13. The Structure of Silica Whiskers

H. C. Duecker and W. K. Haller,

Glass Section

Whisker-shaped fibers of silica have been grown by passing a stream of nitrogen, silicon tetrafluoride, and water vapor over a platinum target heated to 1200°C. X-ray and electron diffraction studies of the pristine whiskers did not give any indications of crystallinity, although X-ray diffraction patterns have been obtained for the three main crystalline forms of silica by devitrifying the whiskers in a proper manner. Electron-microscopic studies indicate that very young and small whiskers at 50,000 X have much the same appearance during the earliest observable stages of growth as the older and larger ones have at only 500 X. Since all the above observations, and optical observations as well, indicate an amorphous structure, radial distribution studies of the whiskers are being made using monochromatic X-ray diffraction data. It is hoped that this study will aid in the determination of possible structural arrangements, thereby making it possible to assign either an amorphous or transitional structure to the whiskers. From this assignment it should be possible to obtain a better comparison of the vitreous and crystalline forms of silica.

### 5.14. Structure Models for Amorphous and Crystalline Phases of Simple Substances

Fred Ordway, Crystal Growth Section

Structure models have been built by a well defined logical process that represents approximately the real process of condensation. Models with tetrahedral coordination, built in this way, are crystalline if a minimum nucleus of crystalline structure is present initially, but are amorphous otherwise. The statistical geometry and topology of the amorphous models is being studied.

### 5.15. Radial-Distribution Studies of Glasses

S. Block and G. J. Piermarini,

Crystallography Section

In connection with a study of immiscibility, models were proposed for the cation-modifier distribution in borate and silicate glasses. On the basis of these models certain interatomic vectors are expected. X-ray diffraction studies have been used to obtain independent information about these interatomic vectors. In the past several months radial-distribution studies of strontium borate glasses, in conjunction with previous studies on barium- and cadmium-containing glasses (Piermarini and Block, 1963) have indicated a similarity of cation distribution in all these systems. This short-range order is similar to that found in crystalline  $BaO \cdot 2B_2O_3$ , whose structure has been determined in this laboratory. Future work is planned to explore the limitations of the similarity of cation distribution in the vitreous and crystalline states.

## 6. PARTIAL LIST OF PARTICIPANTS

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

Participants at the Washington Laboratories:

AMBLER, Ernest: Ph.D. Oxford University, 1953; nuclear reactions, low temperature magnetism; Chief, Cryogenics Section, Heat Division. Author Section 4.10  
AMBS, William J.: Ph.D. Catholic University, 1961; corrosion by energetic species, oxide mono-layer formation; Metal Reactions Section, Metallurgy Division. Author Section 2.18



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

BARBER, David J.: Ph.D. University of Bristol, Bristol, England, 1959; dislocations and plastic flow in alkali-halide crystals; Physical Properties Section, Inorganic Solids Division. Author Section 3.1

BASS, Arnold M.: Ph.D. Duke University, 1949; molecular spectroscopy; Heat Division. Author Section 4.21

BECKER, James H.: Ph.D. Cornell University, 1957; optical and transport properties of semiconductors; Atomic Physics Section, Solid State Physics Division. Author Section 4.2

BLOCK, Stanley: Ph.D. Johns Hopkins University, 1955; X-ray crystallography; Crystallography Section, Inorganic Solids Division. Author Sections 5.2, 5.15

BLUNT, Robert F.: Ph.D. Rice University, 1949; optical properties of solids; Solid State Physics Section, Atomic Physics Division. Author Section 3.12

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

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

BROWER, William S.: Verneuil process; Crystal Growth Section, Inorganic Solids Division. Author Section 2.1

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

BRUMBERGER, Harry: Ph.D. Brooklyn Polytechnic Institute, 1955; low-angle X-ray scattering, critical phenomena and structure of liquids; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Section 5.5

BURLEY, Gordon: Ph.D. Georgetown University, 1962; crystallography of silver iodide; Crystallography Section, Inorganic Solids Division. Author Section 5.11

CALVERT, Joan P.: Growth of oxide films; Metal Reactions Section, Metallurgy Division. Author Section 3.2

CHANG, Te-Tse: Ph.D. University of Colorado, 1962; magnetic resonance; Solid State Physics Section, Atomic Physics Division. Author Section 4.16

COHEN, Martin I.: X-ray diffraction studies of crystals grown at high temperatures; Solid State Physics Section, Atomic Physics Division. Author Section 2.2

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

DESLATTES, Richard D.: Ph.D. Johns Hopkins University, 1959; X-ray spectroscopy; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Section 3.7

DICKSON, Robert W.: Theory of the effect of homogeneous stress on the symmetry of common oxide structures; optical properties of inorganic solids; Physical Properties Section, Inorganic Solids Division. Author Sections 3.11, 4.14

DUECKER, Heyman, C.: Physical chemistry of glasses; Glass Section, Inorganic Solids Division. Author Section 5.13

EARLY, James G.: Ph.D. Rennsalaer Polytechnic Institute, 1963; Kinetics of Crystallization; Metal Physics Section, Metallurgy Division. Author Section 2.4

EISENSTEIN, Julian C.: Ph.D. Harvard University, 1948; low temperature magnetism; Cryogenics Section, Heat Division. Author Section 4.8

ESCALANTE, Edward: Field-emission; Metal Reactions Section, Metallurgy Division. Author Section 2.18

FARABAUGH, Edward N.: Etch-pits; Crystal Growth Section, Inorganic Solids Division. Author Section 2.13

FORMAN, Richard A.: Nuclear and quadrupolar resonance; Solid State Physics Section, Atomic Physics Division. Author Section 4.16

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

FREDERIKSE, Hans P. R.: Ph.D. Leiden University, Netherlands, 1950; semiconductors at low temperatures; Chief, Solid State Physics Section, Atomic Physics Division. Author Section 4.2

FRENCH, Judson C.: Solid state devices and materials; Electron Devices Section, Instrumentation Division. Author Section 3.6

FROLEN, Lois J.: Ph.D. Pennsylvania State University, 1963; spectroscopy, crystallography, microscopy; Pure Substances Section, Analytical and Inorganic Chemistry Division. Author Section 2.8

GLASGOW, Augustus R.: D.Sc. University of Brussels, 1957; preparation and purification of polymeric forms, phase equilibria, purity determinations at high pressures; Pure Substances Section, Analytical and Inorganic Chemistry Division. Author Section 5.10

GORNICK, Fred: Ph.D. University of Pennsylvania, 1959; physical chemistry of high polymers; Macromolecules Synthesis and Structure Section, Polymers Division. Author Sections 2.8, 5.12.

GRABNER, Ludwig H.: Ph.D. Columbia University, 1950; semiconductors, photoconductivity; Solid State Physics Section, Atomic Physics Division. Author Section 3.12

GREENSPAN, Martin: Ultrasonics, mechanics; Sound Section, Mechanics Division.

HALLER, Wolfgang K.: Ph.D. University of Vienna, 1950; physical chemistry of glasses; Glass Section, Inorganic Solids Division. Author Section 5.13

HARDY, Stephen C.: Vapor growth of metal crystals; Metal Physics Section, Metallurgy Division. Author Section 2.17

HARMAN, George G.: Solid state physics, surface phenomena and electroluminescence; Electron Devices Section, Instrumentation Division. Author Section 3.6

HIGIER, Theodore: Semiconductor physics; Electron Devices Section, Instrumentation Division.

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

HORTON, Avery T.: Crystal growth, impurity retention; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Section 2.5

HOWARD, Frank L.: Ph.D. University of Maryland, 1938; Chief, Pure Substances Section, Analytical and Inorganic Chemistry Division.

HOWARD, Robert E.: Ph.D. Oxford, England, 1957; theoretical physics; Metal Physics Section, Metallurgy Division. Author Section 2.16

HUDSON, Ralph P.: Ph.D. Oxford University, 1949; low temperature magnetism; Chief, Heat Division. Author Section 4.5

KAESER, Robert S.: Low temperature magnetism, cryogenics; Cryogenics Section, Heat Division. Author Section 4.10

KAHN, Arnold H.: Ph.D. University of California, 1955; band structure of rutile crystals, studies of paramagnetic impurities in rutile crystals; Solid State Physics Section, Atomic Physics Division. Author Section 4.6

KHOURY, Fred: Ph.D. Leeds University, 1956; morphology and crystallization of polymers; Polymer Physics Section, Polymer Division. Author Section 2.6

KRUGER, Jerome: Ph.D. University of Virginia, 1953; corrosion reactions at metal surfaces; Metal Reactions Section, Metallurgy Division. Author Sections 3.2, 3.4

LaVILLA, Robert E.: Ph.D. Cornell University, 1960; study of transient phenomena by diffraction techniques; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Section 5.4

LEVIN, Ernest M.: Phase equilibria of oxide systems; Crystallography Section, Inorganic Solids Division. Author Section 5.1

LIPPINCOTT, Ellis R.: Ph.D. Johns Hopkins University, 1947; infrared spectroscopy; Crystallography Section, Inorganic Solids Division. Author Section 5.7

MANGUM, William: Ph.D. University of Chicago, 1961; low temperature magnetism; Cryogenics Section, Heat Division. Author Section 4.15

MANN, David E.: Ph.D. University of Chicago, 1948; spectroscopy; Chief, Molecular Spectroscopy Section, Physical Chemistry Division. Author Section 4.22

MARGOSHES, Marvin: Ph.D. Iowa State University, 1953; spectrographic analysis; Spectrochemistry Section, Analytical and Inorganic Chemistry Division. Author Sections 3.9, 3.10

MARSHAK, Harvey: Ph.D. Duke University, 1955; nuclear reactions, cryogenics; Cryogenics Section, Heat Division. Author Section 4.10

MARVIN, Robert S.: Ph.D. University of Wisconsin, 1949; Chief, Rheology Section, Mechanics Division.

MAUER, Floyd A.: Instrumentation for crystallography; Crystallography Section, Inorganic Solids Division. Author Section 3.13

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

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

MILLIGAN, Dolphus E.: Ph.D. University of California, Berkeley, 1958; molecular spectroscopy; Molecular Spectroscopy Section, Physical Chemistry Division.

NEUMAN, Roslyn C.: Properties of polymers; Dielectrics Section, Electricity Division. Author Section 2.7

OGBURN, Fielding: Electrochemistry, electrodeposition; Electrolysis and Metal Deposition Section, Metallurgy Division. Author Section 2.10

ONDIK, Helen M.: Ph.D. Johns Hopkins University, 1957; crystallography, inorganic chemistry; Crystallography Section, Inorganic Solids Division. Author Section 5.2

ORDWAY, Fred: Ph.D. California Institute of Technology, 1949; studies in X-ray crystallography; Chief, Crystal Growth Section, Inorganic Solids Division. Author Sections 2.1, 5.14

OREM, Theodore: Mechanisms of corrosion processes; Metal Reactions Section, Metallurgy Division. Author Sections 2.3, 2.20

OSER, Hans J.: Ph.D. University of Freiburg, 1957; boundary value problems; Applied Mathematics Division. Author Section 2.16

PARETZKIN, Boris: Study of perfection of single crystals by means of X-ray diffraction; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Section 3.14

PARKER, Robert L.: Ph.D. University of Maryland, 1960; growth of crystals; Metal Physics Section, Metallurgy Division. Author Sections 2.3, 2.4, 2.9, 2.15, 2.16, 2.17, 3.3

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

PAYNE, Richard E.: Nuclear resonance; Solid State Physics Section, Atomic Physics Division. Author Section 4.16

PEISER, H. Steffen: Crystallography and crystal chemistry; Chief, Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Sections 3.14, 4.14

PERLOFF, Alvin: Structure analysis; Crystallography Section, Inorganic Solids Division. Author Section 5.2

PFEIFFER, Earl R.: Crystal growth from solution; Cryogenics Section, Heat Division. Author Section 4.9

PIERMARINI, Gaspar J.: Radial distribution studies; high pressure x-ray diffraction studies; Crystallography Section, Inorganic Solids Division. Author Sections 5.6, 5.15

POLLACK, Gerald L.: Ph.D. California Institute of Technology, 1962; low temperature physics; Crystal Growth Section, Inorganic Solids Division. Author Sections 2.13, 2.14, 3.8

POWERS, Joseph: Ph.D. University of Massachusetts, 1961; kinetics, morphology, and mechanism of crystallization of polymers; Macromolecules Synthesis and Structure Section, Polymers Division. Author Sections 2.7, 3.15, 5.8

PROCTOR, Thomas M.: Solid state physics; Sound Section, Mechanics Division. Author Section 4.1

QUINN, Fred A.: Crystallization rate of high polymers; Macromolecules Synthesis and Structure Section, Polymers Division. Author Sections 3.15, 5.8

RASBERRY, Stanley D.: Spectrographic analysis; Spectrochemistry Section, Analytical and Inorganic Chemistry Division. Author Sections 3.9, 3.10

RAYBOLD, Richard L.: Solid state physics; surface phenomena and electroluminescence; Electron Devices Section, Instrumentation Division.

READ, Susan F. J.: Ph.D. Oxford University, 1963; solid state physics; Temperature Physics Section, Heat Division. Author Section 4.12

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

ROBERTS, D. Ellis: Crystal growth; Solid State Physics Section, Atomic Physics Division. Author Section 2.2

ROBINSON, Henry E.: Thermal conductivity measurement on solids at high and low temperatures; Chief, Heat Transfer Section, Building Research Division.

ROSS, Gaylon S.: Nucleation, crystal growth; Pure Substances Section, Analytical and Inorganic Chemistry Division. Author Section 2.8

ROTH, Robert S.: Ph.D. University of Illinois, 1951; X-ray diffraction studies in connection with phase equilibria; Crystallography Section, Inorganic Solids Division. Author Section 5.1

RUBIN, Robert J.: Ph.D. Cornell University, 1951; theoretical chemical physics; Heat Division. Author Section 4.7

RUBIN, Sherwin: Hall-effect devices and materials; Engineering Electronics Section, Instrumentation Division. Author Section 4.3

RUFF, Arthur W.: Dislocations and etch pits; Metal Physics Section, Metallurgy Division. Author Section 2.21

RUTHBERG, Stanley: Materials and physics of vacuum devices; Electron Devices Section, Instrumentation Division.

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

SCHAFFT, Harry A.: Semiconductor devices and breakdown phenomena; Electron Devices Section, Instrumentation Division. Author Section 3.6

SCHNEIDER, Samuel J.: Phase equilibria of oxide systems and metal oxide melting point standards; Crystallography Section, Inorganic Solids Division. Author Section 4.13

SCHOOLEY, James F.: Ph.D. University of California, 1961; crystal growth for low-temperature paramagnetic studies; Cryogenics Section, Heat Division. Author Section 4.9

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

SCHROEDER, Rudolph A.: Ph.D. University of Maryland, 1957; infrared spectroscopy; Crystallography Section, Inorganic Solids Division. Author Section 5.7

SCRIBNER, Bourdon F.: Analytical applications of optical and X-ray spectroscopy; Chief, Spectrochemistry Section, Analytical and Inorganic Chemistry Division. Author Section 3.9, 3.10

SIMMONS, John S.: Ph.D. University of California, 1961; mathematical physics; Director's Office. Author Section 2.16

SPINNER, Sam: Elastic properties of inorganic solids; Physical Properties Section, Inorganic Solids Division. Author Section 3.5

STRASSBURGER, John: Crystal growth from solution; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Section 2.5

SWANSON, Howard E.: Physical chemistry, X-ray diffraction; Crystallography Section, Inorganic Solids Division. Author Section 5.3

SWARTZENDRUBER, Lydon J.: Solid state physics; Electron Devices Section, Instrumentation Division. Author Section 3.6

TIGHE, Nancy: Defects by means of electron microscopy of non-metallic crystals; Physical Properties Section, Inorganic Solids Division. Author Section 3.1

TORGESEN, John L.: Ph.D. Columbia University, 1942; crystal growth, impurity retentions, crystal properties; Crystal Chemistry Section, Analytical and Inorganic Chemistry Division. Author Section 2.5

THURBER, Willis R.: Thermoelectricity; Solid State Physics Section, Atomic Physics Division.

VACHER, Herbert C.: X-ray diffraction; Metal Physics Section, Metallurgy Division. Author Section 2.3

VAN VALKENBURG, Alvin: High pressure transitions; Crystallography Section, Inorganic Solids Division. Author Section 5.9

WACHTMAN, John B.: Ph.D. University of Maryland, 1961; mechanical and electrical properties of crystals; Physical Properties Section, Inorganic Solids Division. Author Sections 3.5, 4.14

WAGNER, Timothy: Growth and evaporation of whiskers; Metal Physics Section, Metallurgy Division. Author Section 2.15

WASILIK, John H.: Ph.D. Catholic University, 1956; dielectric constant and losses, ultrasonics; Solid State Physics Section, Atomic Physics Division. Author Section 4.4

WEIR, Charles E.: Infrared spectroscopy and high pressure physics; Crystallography Section, Inorganic Solids Division. Author Sections 5.6, 5.7

WILL, Richard S.: Electron-field emission; Electron Physics Section, Atomic Physics Division. Author Section 4.20

YOLKEN, Howard T.: Growth of oxide films; Metal Reactions Section, Metallurgy Division. Author Section 3.2

YOUNG, Russell D.: Ph.D. Pennsylvania State University, 1959; surface physics, particularly with the field-emission microscope; Electron Physics Section, Atomic Physics Division. Author Sections 4.19, 4.20

#### Participants in the Boulder Laboratories:

COOK, Alan R.: Physical instrumentation; Radio and Microwave Materials Section, Radio Standards Physics Division. Author Section 4.17

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

GRUZENSKY, Paul M.: Ph.D. Oregon State College, 1959; physical chemistry and high purity materials; Radio and Microwave Materials Section, Radio Standards Physics Division. Author Section 2.12

GUNTNER, Charles S.: Imperfections, flow and fracture, phase transformations; Properties of Materials Section, Cryogenics Engineering Laboratory. Author Section 2.11

- JEFFERSON, Clinton F.: Ph.D. University of Michigan, 1959; solid state solutions for ferri-magnetic characteristics; Radio and Microwave Materials Section, Radio Standards Physics Division. Author Section 4.17
- MATARRESE, Lawrence M.: Ph.D. University of Chicago, 1954; solid state physics, EPR and other resonance spectroscopy related to solid state mechanisms; Radio and Microwave Materials Section, Radio Standards Physics Division. Author Section 2.11
- REED, Richard P.: Imperfections, flow and fracture, phase transformations; Properties of Materials Section, Cryogenics Engineering Laboratory. Author Section 4.18
- RISLEY, Alan S.: Magnetism and ferrites; Radio and Microwave Materials Section, Radio Standards Physics Division. Author Section 4.17
- WELLS, Joseph S.: Microwave physics, solid state physics as it relates to ENDOR and NMR; Radio and Microwave Materials Section, Radio Standards Physics Division. Author Section 4.17

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- R. A. Forman and D. R. Lide, Jr. (1963); Quadrupole Coupling Constants from the Microwave Spectrum of Hydrazoic Acid, J. Chem. Phys. (accepted).
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J. F. Schooley, D. D. Hoppes, and A. T. Hirshfeld (1962); The Gamma-Ray Distribution from Oriented Cerium-141, J. Research, Nat'l Bur. Standards 66A, p. 317.

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H. E. Swanson, M. C. Morris, R. P. Stinchfield, and E. H. Evans (1963); Standard X-Ray Diffraction Powder Patterns, Nat'l Bur. Standards Monograph 25 Section 2.

L. J. Swartzendruber (1963); Applications of a Semiconductor Surface-State Charge-Storage Device, Solid State Electronics 6, p. 59.

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A. Van Valkenburg and J. Powers (1963); Optical Observations of Pressure Induced Transitions in Polymers, J. Appl. Phys. 34, p. 2433.

J. B. Wachtman, Jr. (1963); Mechanical and Electrical Relaxation in  $\text{ThO}_2$  Containing  $\text{CaO}$ , Phys. Rev. 131, No. 2.

J. B. Wachtman, Jr., H. S. Peiser, and E. P. Levine (1963); Symmetry Splitting of Equivalent Sites in Oxide Crystals and Related Mechanical Effects, J. Research, Nat'l Bur. Standards 67A, p. 281.

J. B. Wachtman, Jr., W. E. Teeft, and D. G. Lam, Jr. (1962); Elastic Constants of Rutile ( $\text{TiO}_2$ ), J. Research, Nat'l Bur. Standards 66A, p. 465.

J. B. Wachtman, Jr., Mary L. Wheat, and S. Marzullo (1963); A Method for Determining the Elastic Constants of a Cubic Crystal from Velocity Measurements in a Single Arbitrary Direction; Application to  $\text{SrTiO}_3$ , J. Research, Nat'l Bur. Standards 67A, p. 193.

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## THE NATIONAL BUREAU OF STANDARDS

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

### WASHINGTON, D. C.

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

**Metrology.** Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Volume.

**Heat.** Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics.

**Radiation Physics.** X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

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

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

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

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

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

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

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

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

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

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

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

**Office of Weights and Measures.**

### BOULDER, COLO.

#### CRYOGENIC ENGINEERING LABORATORY

Cryogenic Processes. Cryogenic Properties of Solids. Cryogenic Technical Services. Properties of Cryogenic Fluids.

#### CENTRAL RADIO PROPAGATION LABORATORY

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

**Troposphere and Space Telecommunications.** Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Spectrum Utilization Research. Radio-Meteorology. Lower Atmosphere Physics.

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

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

#### RADIO STANDARDS LABORATORY

**Radio Standards Physics.** Frequency and Time Disseminations. Radio and Microwave Materials. Atomic Frequency and Time-Interval Standards. Radio Plasma. Microwave Physics.

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

**Joint Institute for Laboratory Astrophysics-NBS Group (Univ. of Colo.).**

