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Technical Note

251

RESEARCH ON CRYSTAL GROWTH AND CHARACTERIZATION AT THE NATIONAL BUREAU OF STANDARDS JANUARY TO JUNE 1964



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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* NBS Group, Joint Institute for Laboratory Astrophysics at the University of Colorado.

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NATIONAL BUREAU OF STANDARDS

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ISSUED OCTOBER 19, 1964

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Edited by Howard F. McMurdie
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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RESEARCH ON CRYSTAL GROWTH AND CHARACTERIZATION

AT THE NATIONAL BUREAU OF STANDARDS

JANUARY TO JUNE 1964

Edited by

H. F. McMurdie

Abstract

The National Bureau of Standards with partial support from the Advanced Research Projects Agency of the Department of Defense is continuing a wide program of studies involving crystalline materials. These include investigation of methods and theory of growth, study of detection and effects of defects, determination of physical properties, refinement of chemical analysis, and determination of stability relations and atomic structure. The types of materials range from organic compounds, through metals, and inorganic salts to refractory oxides. This Technical Note, the fourth in the series, summarizes the progress of these various projects from January to June, 1964, and lists the related publications and participating scientists.

1. INTRODUCTION

This is the fourth biannual report on crystal research at the National Bureau of Standards. The three preceeding ones have been published as NBS Technical Notes 174, 197, and 236. These publications present the background of the NBS effort in this area. Much of the work described here is carried out with the support of the Advanced Research Projects Agency. In anticipation of future technological demands in crystal and material science, ARPA is encouraging the NBS to study the techniques and theory of crystal growth, to characterize precisely the crystals produced by various methods, and to extend precision measurement to physical and chemical properties of crystals. The Bureau's own program in many aspects of this field is extensive and no effort is made in the research descriptions below to separate the two efforts. Only in the few instances in which financial support from other agencies contributed to the program is an acknowledgement given.

The increase of the effort in crystal science by the ARPA cooperation has resulted in an increased number of contacts and cross-linking between participants in the program. This is a result in some cases of having regularly scheduled group discussions of common problems and an exchange of visitors with other crystal science centers. The program as a whole at the National Bureau of Standards is under the direction of Dr. Harry C. Allen, Jr.

We wish to acknowledge the editorial assistance of Miss Lois L. Bardeen and Miss Betty L. Rugins of the Inorganic Materials Division and the help given by the assistant editors who have represented the Bureau Divisions as follows:

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Radio Standards Physics	J. L. Dalke

2. CRYSTAL GROWTH

This chapter is concerned with mechanisms and techniques of crystal growth and dissolution.

2.1 Growth of Dislocation-Free Metals from the Melt

T. H. Orem, Crystallization of Metals Section

R. W. Dickson, Physical Properties Section

and

R. L. Parker, Crystallization of Metals Section

The background of this work is given in NBS Technical Notes 174, Section 4.3, 197, Section 2.3, and 236, Section 2.1.

During the first three months of this reporting period, considerable work was done in photographing, by the Lang technique, aluminum crystals pulled from a melt of 99.999% initial purity. Since it was considered a possibility that much of the observed imperfections in the topographs was due to surface strains and other surface imperfections in the carrot-shaped crystals, they were studied both in the "as-grown" condition and after deep etching with aqua-regia to remove surface material. Approximately 25 photographs were taken on three such crystals, some of which received several etchings with photographing after each etching. There were no significant differences between the etched and unetched crystals.

A considerable amount of work was done on an Al crystal received from the Battelle Institute. The crystal had been pulled from a high-purity melt and had little visible oxide on its surface. It thus had a

very smooth bright surface. A total of 49 photographs were taken of this crystal but no significant results obtained, due partly to the fact that the crystal had considerable substructure.

A number of aluminum crystals were pulled from a melt of 99.9999% initial purity (zone-refined) during this period. It is believed that the use of the higher-purity aluminum, coupled with an improvement in the crystal-pulling furnace, which minimized oxidation of the melt during the crystal-pulling process, has contributed significantly to the production of better crystals.

Of approximately a dozen crystals grown, from the higher-purity Al, using both monocrystalline and polycrystalline starting-seeds, two are believed to be of significant interest and are shown here. Figure 1 is a Lang topographic photograph of the tip of a crystal of near [001] orientation. The decrease in dislocation density near the tip is obvious. Further along the crystal, the dislocation density increased conspicuously. Figure 2 is a crystal grown in such a manner that its axis is parallel to [111]. Note the conical helix at the end of the high-imperfection (white) area. The pitch of the screw-like configuration approximates that of the crystal-pulling rate per revolution of the pulling shaft. The low dislocation-density area of this crystal extends inward from the tip of the crystal to the apex of the conical helix, a distance of ≈ 1.6 mm, at which point the diameter is $\approx .4$ mm. The crystals used to obtain Figures 1 and 2 are the only Al ones we have grown and examined which show a contrast in reflection intensity near the tip such that individual dislocations can be resolved. They both show that there is a critical diameter above which the imperfections are so dense as to be incapable of resolution. Both topographs were obtained by use of the Rigaku-Denki microfocuss X-ray unit and camera. Other investigators have found that in the growth of carrot-shaped aluminum crystals by pulling from the melt, .5 mm is the diameter below which a crystal will exhibit a decrease in dislocation density.

Confirmation of the configuration in the tip of the crystal in Figure 2 may be seen in Figure 3, a double-crystal diffraction topograph of the same area of the crystal, taken by R. D. Deslattes, Crystal Chemistry Section.

Current work involves the production and characterization of additional aluminum crystals with a view toward further investigation of this crystal diameter effect.

2.2 Kinetics of Growth of Crystals from the Melt

J. G. Early and R. L. Parker,

Crystallization of Metals Section

As stated in previous technical notes (see NBS Technical Notes 174, Section 4.4, 197, Section 2.4, and 236, Section 2.2), the objective of this project is to study the kinetics of the growth of a solid from the melt, and to correlate this with the effect of crystal orientation.

Several experiments have been made with a single crystal of tin grown from tin having an as-received purity of 99.999%. The results seem to indicate that sufficient solute is being rejected into the liquid at the solid-liquid interface to cause constitutional supercooling which partially masks the kinetic effects at the interface. Further experiments are planned using 99.9999% tin as the raw material for



Fig. 1. Lang topographic photograph of the tip of an Al crystal with the axis parallel to $[001]$ direction.



Fig. 2. Lang topographic photograph of the tip of an Al crystal with the axis parallel to $[111]$.

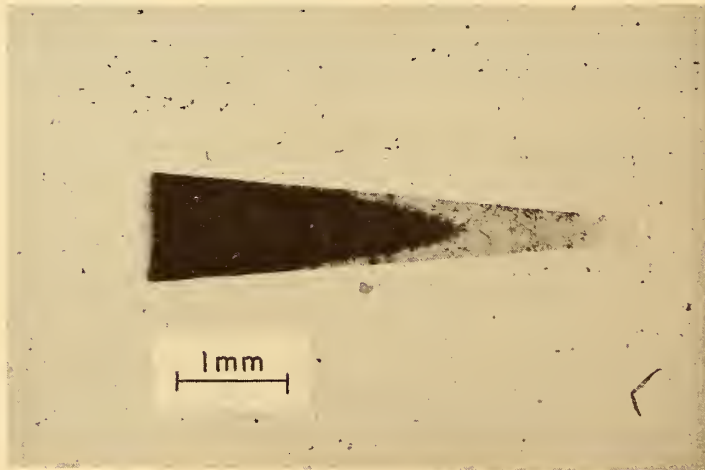


Fig. 3. A double-crystal diffraction topograph of the crystal shown in Figure 2.

growing additional single crystals in an effort to eliminate solute effects. In addition, a zone-refining apparatus is being purchased to aid in the preparation of high-purity materials for subsequent experiments.

2.3 Theory of Dendritic Crystallization

S. R. Coriell and R. L. Parker,

Crystallization of Metals Section

In a recent article, Mullins and Sekerka [J. Appl. Phys., 34, 323 (1963)] have studied the stability of shape of a spherical particle growing in a supersaturated solution or a supercooled liquid. They found that when the radius of the sphere exceeded a certain radius R_c the spherical shape was not stable. A question arises as to whether this type of instability can explain the formation of branches on dendrites. Sufficiently far from the dendrite tip, the dendrite shape may be approximated as a cylinder. We have studied the stability of shape of an infinite cylinder using the method of Mullins and Sekerka. It is found that the circular cross-section of a cylinder is stable when its radius is below, and unstable when its radius is above a certain radius R_c . This is analogous to the result for a sphere. For the cylinder, however, R_c is a function of the supercooling, while for the sphere, R_c is independent of the supercooling. It is also found that the cylinder is always unstable with respect to certain perturbations which decrease the surface to volume ratio of the cylinder. An article, "Stability of a Cylinder Growing in a Diffusion Field", has been prepared for publication. (Coriell and Parker, 1964)

The preceding treatment assumes local equilibrium at the interface and that the surface free energy is isotropic. It would be highly desirable to study the stability of shapes without these assumptions. The possibility of applying the Mullins and Sekerka method to the stability of a more realistic shape (e. g. a parabola of revolution) is being considered.

2.4 Crystal Growth Studies by Electron Field Emission Techniques

S. C. Hardy and R. L. Parker,

Crystallization of Metals Section

The heterogeneous nucleation of Hg crystals from the vapor phase is being studied in an electron field emission microscope. The W field emission tip provides the substrate upon which the nuclei grow. The stable nuclei appear as bright spots superposed on the pattern from the tip. The emission patterns of a clean W tip and of the same tip after nucleation has occurred are shown in Figures 4 and 5, respectively. Nucleation takes place about, but not on, the 011 and 112 type planes. The nuclei are cap-shaped. The time required to form nuclei is being measured over a range of vapor pressures and substrate temperature.

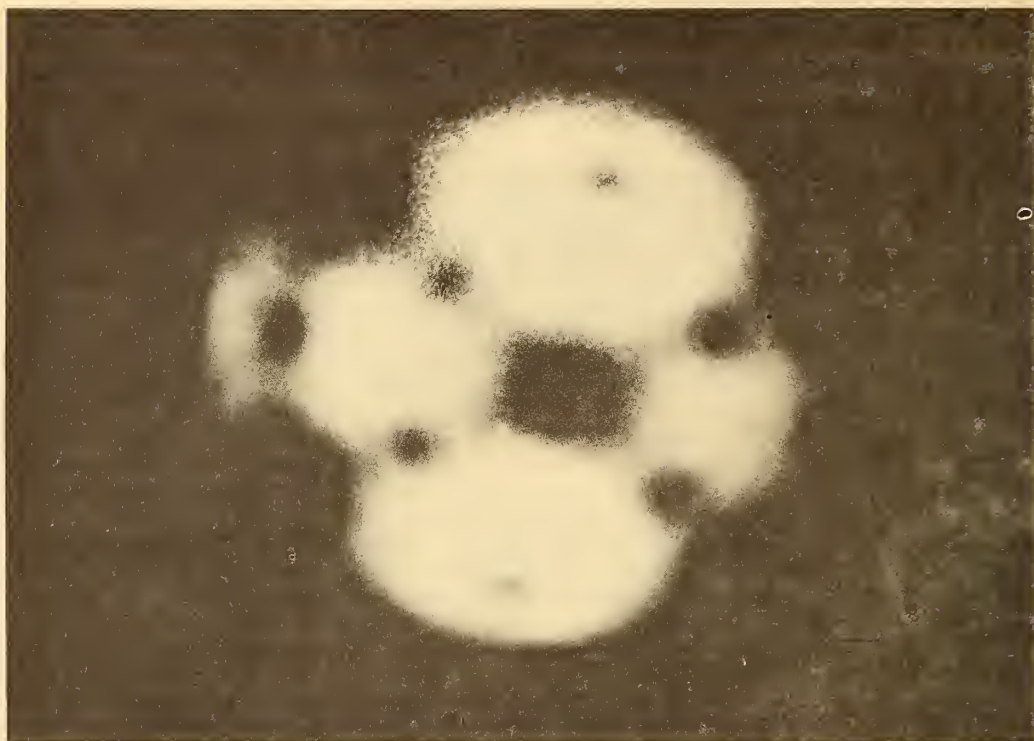


Fig. 4. Emission pattern of a clean W tip.

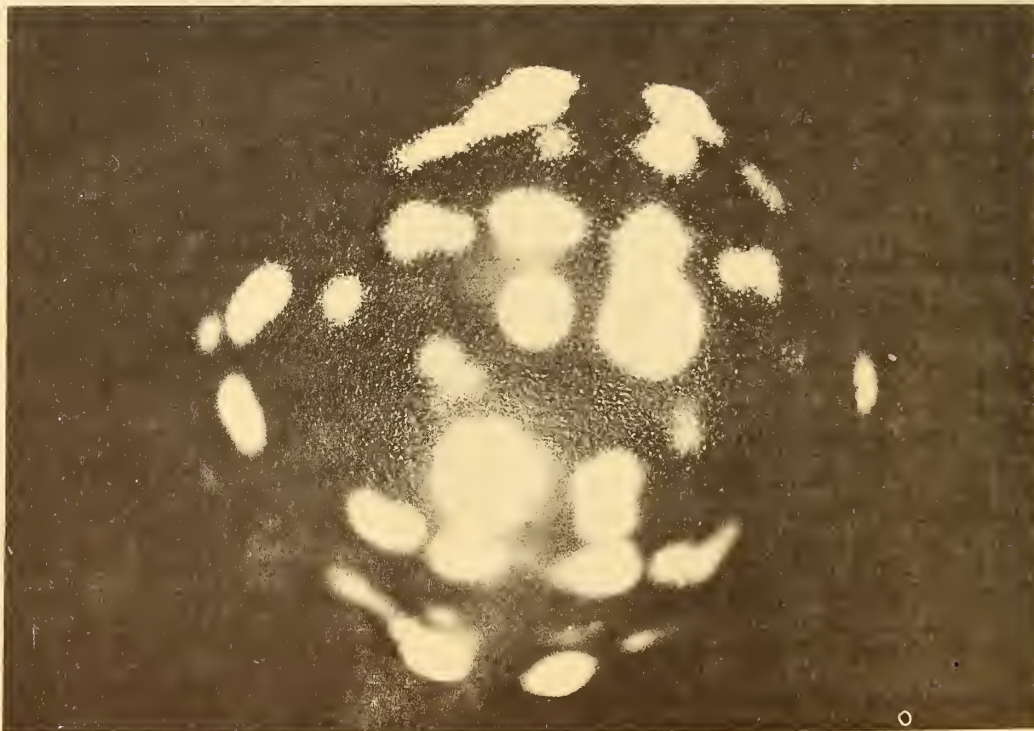


Fig. 5. Emission pattern of the same W tip as Figure 4 after nucleation of Hg has occurred.

2.5 Field-Emission Microscopy of Crystal Growth Processes

A. J. Melmed,
Corrosion Section

The writer began work at the National Bureau of Standards in March, 1964. Laboratory facilities have been constructed and tested, and experimental work begun. Two investigations are in progress: (1) A study of the epitaxial growth of Fe crystals, from the vapor phase, on W field emitters, and (2) Measurements of the activation energy for Cu surface self-diffusion from the field-deformation and from zero field annealing rates of Cu crystals epitaxially grown on W field emitters.

2.6 High-Temperature Crystal Growth*

W. S. Brower,
Crystal Chemistry Section

The use of direct electromagnetic heating using high frequency RF power has been successfully used to heat NiO to its melting point. This heating method has been used to pass molten zones through polycrystalline NiO rods in the usual floating zone arrangement. Some NiO rods have been zoned a total of eight passes, with no significant improvement in crystallite size from the first to last pass. Current efforts are being directed toward reducing the thermal cracking and improving the temperature control in order to obtain single crystals.

Crystal growth is underway with the use of the Verneuil' technique. In particular, pre-oriented crystals of chromium-doped rutile, TiO_2 , have been grown.

2.7 Crystal Growth from Solution

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

The growth of large single crystals from solution by temperature-program techniques (see NBS Technical Notes 174, Section 4.5, 197, Section 2.5, and 236, Section 2.8) has been continued with the production of specimens of ammonium dihydrogen phosphate and sodium chlorate. Grown in the presence of Cu^{++} ion impurity, sodium chlorate undergoes a marked change in habit with the {110} and {111} forms in much greater predominance than characteristic of growth from pure solution. Although it was reported previously (NBS Technical Note 236, Section, 2.8) that some differences in Cu^{++} deposition occur dependent on growth direction, more precise analysis of recently harvested crystals show this is not the case. From solution containing 0.18 weight percent Cu^{++} ion, deposition of Cu^{++} on {100}, {110}, and {111} amounts to

* This work is partially supported by the Atomic Energy Commission.

0.6 (± 0.2) ppm with no significant differences outside the precision of the analysis to be noted for these three regions of the crystals.

Potassium acid phthalate (KAP) single crystals are presently being grown by temperature-dropping and isothermal techniques. The goal is to produce crystals of adequate size and perfection for long-wave length X-ray spectroscopy (compare Section 4.15). In an effort to avoid damage to seed crystals by drilling or gluing (for mounting purposes) and to produce crystals as nearly strain-free as possible, seed crystals are grown directly on Teflon sleeve mounts, which are then transferred to the crystal tree for further growth in the large crystal baths. Volunteer growth has been troublesome, especially in the isothermal solvent-evaporation equipment [Karpenko et al., Sov. Phys. Cryst., 6, 120 (1961)]. Excessive nucleation and growth of crystals in the solution surface requires revision of the system to return an appreciable portion of the condensing solvent to the surface, hence decreasing surface supersaturation, to provide a baffle system or to decrease supersaturation in the growth chamber generally [Sampson and Di Pietro, Rev. Sci. Instr. 34, 1150 (1963)].

Characterization of ADP crystals by rocking curves and x-ray diffraction topography (see Section 4.15) has continued with the examination of (100), (101), and (110) sections. The careful preparation of crystal sections by string-sawing with water as the solvent, followed by etch-polishing with ethyl alcohol-water mixtures (80:20 by volume) produces specimens in which high intrinsic perfection is retained. Flat etch-polishing is accomplished by rotating and advancing the crystal specimen closely adjacent to, but not touching, a rotating glass plate over which flows a thin film of the alcohol-water etchant. A photograph of the etch-polish device is shown in Figure 6. The surfaces thus produced possess diffraction characteristics believed to approach those inherent in the crystals as grown and are tentatively taken to be representative of the bulk crystal. The general uniformity of the diffraction topographs shows the absence of significant strain and regions of 1 cm^2 or more to be free of defect images.

It is hoped that etch-pit studies may corroborate the results which have been obtained on crystal perfection of ADP by x-ray methods. Etch-polishing by the procedure noted above, but with 10 drops of saturated solution of ferric chloride in concentrated hydrochloric acid added per liter of alcohol-water etchant, produces etch-pits on {100} illustrated in Figure 7. The pits are well defined, showing tetragonal symmetry with four {101} facets extant. On {101} the same etchant produces triangular etch-pits, shown in Figure 8, defined by three {101} facets. A saturated solution of potassium-acid-phthalate has also proved effective in developing etch-pits on the {100} face of ADP. A momentary dip in the solution, followed by immediate rinsing in isopropyl alcohol, results in etch-pits shown in Figure 9. Good definition and tetragonal symmetry are apparent. A comparison of the patterns and density of etch-pits with those of defect images in x-ray topographs of the same specimens is presently in progress.

Work on the growth of oxalic acid single crystals from solution in glacial acetic acid and in acetone-water mixtures has been concluded. The details of this investigation are reported in a paper (Torgesen and Strassburger, 1964) which has been accepted for publication in Science.



Fig. 6. Etch-polish assembly.

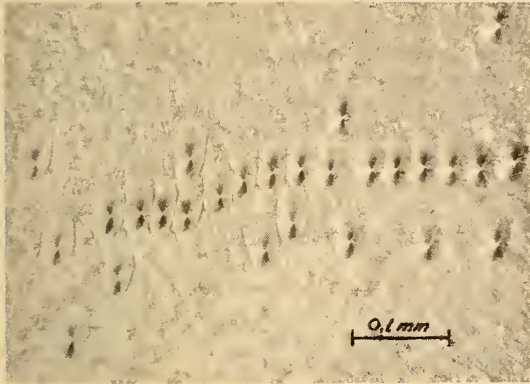


Fig. 7. Etch-pits in ADP [100].
Etchant: Ethyl alcohol-water mixture (80:20 by volume) containing 10 drops per liter of a saturated solution of ferric chloride in conc. hydrochloric acid.



Fig. 8. Etch-pits in ADP [101].
Etchant: Same as for Figure 7.

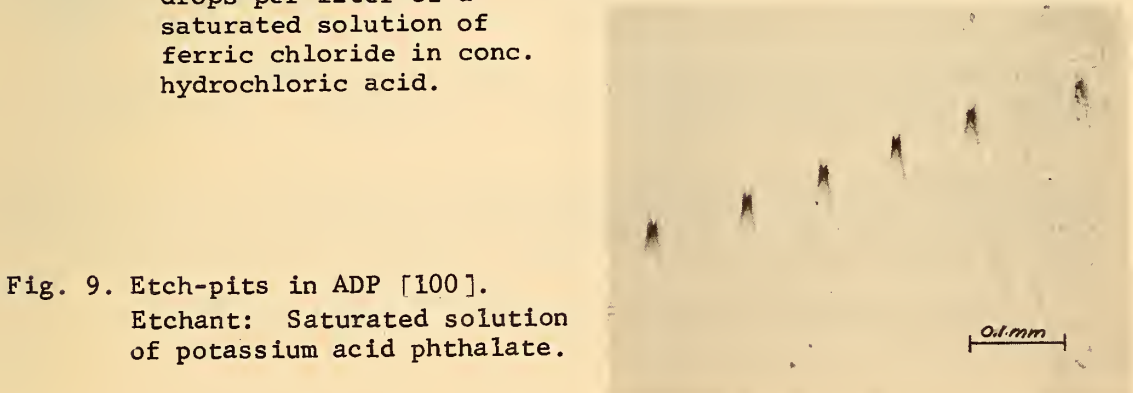


Fig. 9. Etch-pits in ADP [100].
Etchant: Saturated solution of potassium acid phthalate.

2.8 Hydrofluorothermal Growth of Crystalline BeF_2 under HF Pressure

A. R. Glasgow, Jr.,

Analysis and Purification Section

Researches were performed in the development of a "hydrofluorothermal" process for the growth of BeF_2 crystals in a platinum-lined steel bomb under pressures of 30-50 atmospheres of HF. (Tech. Note 197, Section 5.10). This method is similar to the hydrothermal growths of quartz from SiO_2 .

A major bottle-neck in the development of this process has been the anhydrous addition of HF to a closed bomb. The technique under development is the anhydrous addition of HF from a Pt and Pt-Ir ampoule with a thin-rupture disc (.001 inch) of platinum. The HF is added, sealed, and weighed in the ampoule where the pressure never exceeds 2 atmospheres. However, after placement in the closed bomb and heating to 100 to 150 °C, the internal pressure of HF inside the ampoule increases to 10-30 atmospheres. This causes the disc to rupture and the HF to be released to the contents of the bomb.

The necessary Pt and Pt-iridium parts have been received. The technique of transfer and sealing is nearing perfection. Actual growths by this method are expected later this year. A cross-sectional view with a legend describing the parts of the rupture-disc ampoule is shown in the accompanying drawing, Figure 10.

2.9 Crystal Growth and Structure Studies

D. E. Roberts,

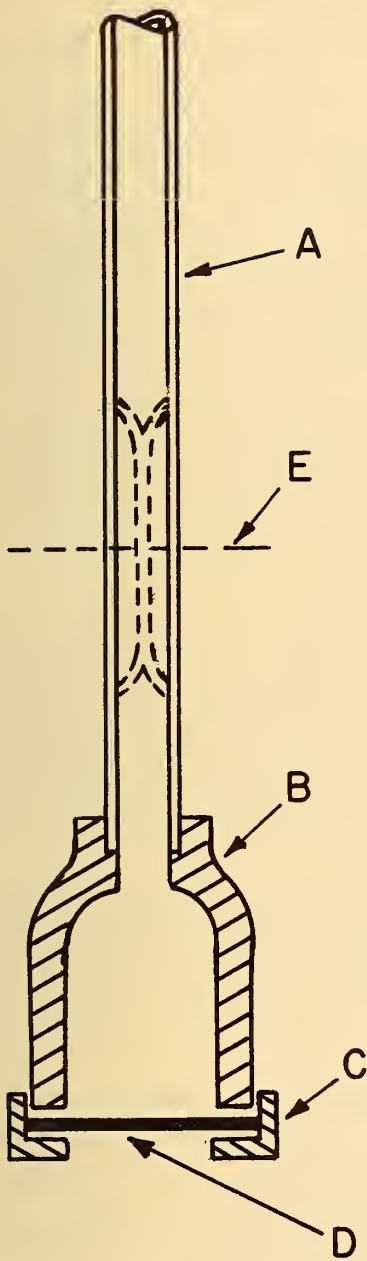
Solid State Physics Section

Single crystals of rutile (TiO_2) are being grown, doped, and prepared as required. Measurements are made of transport, optical, magnetic, mechanical, and resonance properties. Growth is by the flame-fusion technique, but methods of flux or solvent growth are being tried. Dopants include more than 15 elements which have been mixed into the powder from which boules are grown.

A number of materials have been prepared for superconductivity studies. These include Mg_3Bi_2 , SnSe , SnSe_2 , Sb_2Se_3 , InTe_3 , Ag_2Se , AuSb_2 , Bi_2Te_3 , GaTe , and MoO_3 .

Formerly (Tech. Note 236, Section 2.7) we reported CdS crystals grown from the vapor in needle and platelet form up to a few m.m. in dimensions. Because of their adaptability for optical measurement the present effort is being made to obtain platelets of a larger size.

Other vapor-grown materials include CdTe, CdO, and MoO_3 .



- A. Platinum tube 1/8 inch O.D.
.010 inch wall
- B. Platinum-iridium body 90% Pt
and 10% Ir alloy
- C. Platinum-iridium ring 90% Pt
and 10% Ir alloy
- D. Platinum disc, foil .001 inch
thick soldered to B and C
- E. Position where tube is cut off
after filling with HF and clos-
ing tube with pliers

Fig. 10. Rupture-Disc-Ampoule

2.10 Pseudopentagonal Twins in Electrodeposited Copper Dendrites

F. Ogburn,
Electrolysis and Metal Deposition Section,

and

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

This work was described in NBS Technical Note 236, Section 2.17.

The results have since been published (Ogburn, Paretzkin, and Peiser, 1964).

2.11 Crystal Growth of Refractory Phases from Solvents

H. S. Parker,

Crystal Chemistry Section

This project was initiated in December, 1963. The objectives are to develop and evaluate methods of growth of highly perfect crystals at temperatures below the melting point of the crystal. The use of temperatures at or near the melting point of the crystal must unavoidably introduce physical lattice defects from thermal agitation alone. Additionally, crystals of many substances are difficult or impossible to grow at temperatures approaching the melting point because of high vapor pressure, incongruent melting or undesirable phase changes.

The method being considered here involves a traveling solution zone in a specimen placed in a temperature gradient. The method in its essentials, first proposed by Pfann ["Zone Melting", Wiley & Sons, New York, 1958] has been analyzed theoretically by W. A. Tiller [J. of Appl. Phys. 34, 2757-2762 (1963)] and has been applied successfully by A. I. Mlavsky and M. Weinstein [J. of Appl. Phys. 34, 2885-2892 (1963)] to the growth of GaAs and SiC.

The necessary equipment has been assembled and a series of experiments growing zinc oxide are currently in progress. The experimental configuration involves a single-crystal seed of zinc oxide separated from the polycrystalline source material by a solvent layer approximately 0.2 to 0.3 mm in thickness with the resulting "sandwich" placed in a suitable temperature gradient. Of the various solvents investigated, evidence of growth thus far has been obtained only through the use of PbMoO_4 as a solvent, and operating temperatures of the order of 1100 to 1200 °C. Efforts to find more suitable solvents are continuing, and attempts will be made to optimize the solvent thickness and operating temperature using PbMoO_4 .

R. W. Jackson and J. L. Torgesen,

Crystal Chemistry Section

The purpose of this investigation is to study the mechanism of growth of crystals from solution and how it is influenced by supersaturation and the presence of impurities.

Molecules or ions arriving at a crystal face by diffusion from the solution will not be incorporated into the lattice unless a growth step exists on the surface. The old theories of crystal growth [H. E. Buckley, Crystal Growth (John Wiley & Sons, New York, 1951) Chapter 6] suggest that the growth step originates as a surface nucleus, which, when larger than a certain critical size, will grow until the whole face is covered. Growth then ceases until a new surface nucleus is formed. It is known that crystal growth, once initiated can proceed at low supersaturation where the probability of surface nucleation is small. Modern theories [Cabrera and Vermilyea, in Growth and Perfection of Crystals, Doremus, Robert, and Turnbull, eds. (John Wiley & Sons, New York, 1958) p. 393] propose that a continuing source of growth steps is provided by imperfections in the crystal in the form of screw dislocations.

The examination of dry crystal surfaces after growth by reflection-phase-contrast microscopy may fail to reveal growth steps or evidence of dislocations. Only when the growth steps are large and the crystal differs considerably in refractive index from the solution in which it is growing are growth steps visible by transmitted light with the light microscope. A more sensitive method, used successfully to observe growth layers on growing sucrose crystals [Albon and Dunning, Acta. Cryst., 12, 219 (1959)] employs microscopic observations with reflected light. This method is being used in the present investigation to study the growth of ADP crystals from aqueous solution.

Small crystals of ADP are being grown by feeding with supersaturated solution in a special cell, mounted and temperature-controlled on the rotating stage of a microscope. By reflected light and at a magnification of 50X, the surface features of the {100} and {101} faces are being examined during growth. It has been found necessary to use a low-power objective to provide sufficient working distance and the maximum amount of light.

From pure ADP solution, the deposition of crystalline material on {100} proceeds by the movement of spiral steps which are slightly elliptical in shape and emanate from screw dislocation centers. The longer axis of the elliptical spiral appears to be at right angles to the c-axis of the crystal. Photomicrographs of the spirals have been prepared and time-lapse films have been taken, recording the movement of steps across the face. A typical single-dislocation spiral is shown in Figure 11. A Frank-Read source (neighboring screw dislocations of opposite hand) forming closed loops, is shown in Figure 12.

No dislocation centers have been observed so far on the {101} face. Growth on this surface apparently proceeds by the movement of essentially straight steps from the edges of the face towards the center. Figure 13 illustrates the phenomenon.

With chromic ion impurity in the solution, the spiral steps on {100} assume an almost rectangular shape with the longer dimension



Fig. 11. Growth spiral on ADP {100}.



Fig. 12. Frank-Read source on ADP {100}.



Fig. 13. Layer growth on ADP {101}.

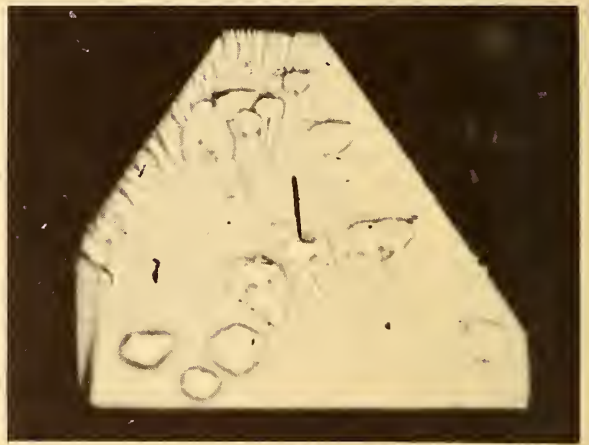


Fig. 14. Dissolution etch-pits on ADP {101}.

again at right angles to the c-axis. At approximately the same supersaturation, the steps move much faster than in pure ADP solution because the number of dislocation sites is considerably increased.

Some observations have been made on the crystal faces during dissolution, the temperature of the growth cell having been raised above the saturation temperature. Etch pits have been seen to occur on both {100} and {101} faces. A typical arrangement on {101} is shown in Figure 14.

2.13 Crystal Growth in Silica-Gel Medium

J. L. Torgesen and A. J. Sober,

Crystal Chemistry Section

Single crystals of salts, sparingly soluble in water, can be grown in silica-gel medium [Holmes, J. Franklin Inst., 184, 743 (1917)] by the slow interdiffusion of the component ions (see Technical Notes 197, Section 2.5, and 236, Section 2.8). The method is most applicable to materials having solubilities in water of the order of 0.01 percent. Copper tartrate, calcium tartrate, lead mono- and di-iodide, and calcium sulfate dihydrate have been grown as single crystals several millimeters in size, some up to 1 cm in longest dimension.

The occlusion of silica in the crystals may occur to a considerable extent. The analysis of copper tartrate single crystals shows the presence of 0.04% silica.

Recent experiments have included the growth of cuprous chloride by the reduction of cupric ion with an appropriate reducing agent in the presence of excess chloride ion. Whereas, as reported previously, the reduction of cupric sulfate by interdiffusion in the silica-gel with hydroxylamine hydrochloride produces both fern-like tetrahedral dendrites of copper metal, the reduction of cupric chloride leads to the growth of crystalline cuprous chloride. The material grows as both fern-like dendrites and as well-developed, optically clear tetrahedra up to 3 mm on edge. An interesting feature is the growth of the dendrites in regions immediately adjacent to the container (pyrex test-tube) walls, the tetrahedra appearing in the more central portions of the gel. Similar results have been obtained with l-ascorbic acid as the reductant, while hydrazine dihydrochloride, contributing to a lower pH in the system, requires initial gels of lower acidity (solubility of cuprous chloride increases in strongly-acid systems). Deaeration of these oxidation-reduction systems with tank nitrogen is being employed to avoid air-oxidation of the reducing agents.

Ways and means to inhibit excessive nucleation (which contributes to large numbers of small crystals) are presently being explored. Although it is recognized that the polymeric silicic-acid chains which comprise the gel may provide nucleation sites in over-abundance, the component solutions of the systems are being ultra-filtered (various pore sizes) to decrease the concentration of motes, which are surely sites for heterogeneous nucleation. In addition, the effects of a "neutral" gel zone (containing initially no reacting ions) between the ion-source regions are under study.

2.14 Spherulitic Growth in Relatively Pure Systems

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

Polymers Division

Studies of both single crystal and spherulitic growth from highly-purified melts of a homologous series of diphenyl alkanes are continuing (see Technical Note 236, Section 2.9). Photomicroscopic observations of supercooled melts of 1, 2 diphenylethane (m.p. 52 °C) 1, 4 diphenylbutane (m.p. 52 °C) and 1, 6 diphenylhexane (m.p. -12 °C) indicate the existence in each case of a maximum growth-velocity with increasing undercooling. It further appears that the spherulitic mode of crystal growth occurs at undercoolings greater than that corresponding to the growth-rate maximum while single crystals have been observed to grow at temperatures closer to the melting point. Some of these observations have been recorded on color film, an edited version of which is available.

The next step in this investigation requires the quantitative determination of growth rates as functions of undercooling. The crystallographic identity of the spherulitic and single-crystal forms has yet to be demonstrated. Attempts to do so are now in progress.

2.15 Homogeneous Nucleation Studies

F. Gornick, G. S. Ross, and

L. J. Frolen,

Polymers Division

During the current report period, a microphotographic facility for time-lapse as well as cinematic photography has been assembled from both commercially-obtained and NBS built components. The purpose to be served by this unit is the photographic observation of freezing in immobilized supercooled liquid droplets on an isothermal hot-stage (see NBS Technical Note 197, Section 2.8). The hot-stage has been tested and shown to be capable of regulation to within 0.01 °C or better for indefinite service in the temperature range 30 ° to 150 °C. A separate report on the performance and details of construction of this hot-stage is now in preparation.

Techniques for the preparation of micron-sized cooled polyethylene droplets are under investigation. Facilities for column fractionation, viscosity determination and high-temperature purification have been acquired and continue to be developed.

A theoretical treatment of the statistics of droplet nucleation in a system subject concurrently to homogeneous and heterogeneous nucleation has been completed and will be submitted for publication in the near future.

2.16 Increase of Thickness with Time of Polyethylene Lamellae Crystallized from the Melt

J. J. Weeks,

Polymers Division

Previously it was assumed that the observed increase of melting temperature of Marlex 50 polyethylene with time of crystallization was a result of thickening of the lamellar crystals [J. J. Weeks (J. Research NBS 67A, 441 (1963))]. Fischer and Schmidt [Angew. Chem. Internat. Edit., 1. 488 (1962)] have obtained x-ray diffraction evidence showing that the low-angle spacing (L_1 and L_2) in bulk polyethylene increases with time of annealing at temperatures above the crystallization temperature, T_x . It was felt that this type of measurement should be made at T_x during^x the crystallization. Using the Kratky low-angle camera, values^x of two spacings were obtained at $T_x = 128.2$ °C as a function of crystallization time on the same Marlex 50 that was used for melting-point studies. The results show that both L_1 and L_2 increase with time during primary (Stage 1) crystallization and then level off. This agrees qualitatively with the melting temperature studies. A short note has been prepared for early publication.

2.17 Aspects of the Mechanism of Spherulitic Crystallization of Polypropylene from Solution

F. Khoury,

Polymer Physics Section

It has been previously reported that isotactic polypropylene crystallizes from $\frac{3}{4}$ % solutions of the polymer in amyl acetate at 115 °C, in the form of pseudopolyhedral aggregates. The habit of these aggregates is similar to that exhibited under the optical microscope by the initial, less accessible, transient structures which develop during the early stages of formation of monoclinic polypropylene spherulites from solution and from the melt (see Technical Note 236, Section 2.14). The determination of the fine structure and mechanism of growth of these model aggregates grown from amyl acetate has been pursued. Further insight into these aspects has been obtained by isolating the aggregates from the mother liquor at an early stage of growth (under isothermal conditions) and subsequently examining them in widely different perspectives under the electron microscope. Electron micrographs representing normal and end-on views of these essentially planar aggregates are shown in Figures 15a and 15b. They possess a distinctly dendritic morphology as clearly revealed in Figure 15a; further, their narrow (150-200Å) diagonally oriented branches exhibit a lamellar habit when viewed along the plane of the aggregates (note the lamellar structures at the extremities of the aggregate shown in Figure 15b).

An acillary study of the birefringence of the aggregates coupled with the structural features briefly summarized folded within the individual branches, the extended interfold-helical segments of the molecules being oriented preferentially parallel to plane of the aggregates and normal to their longer lateral edges. An attempt is being made to

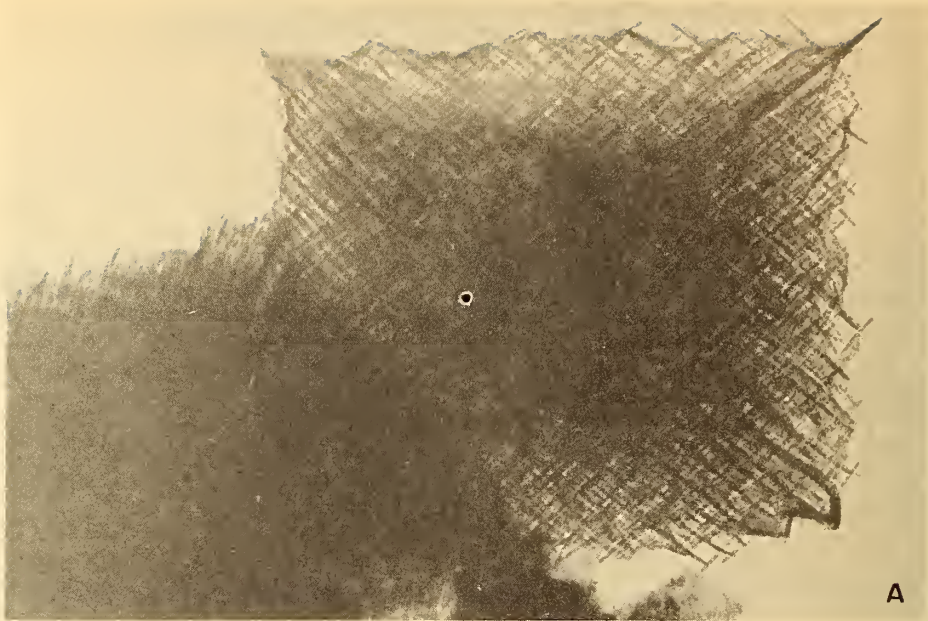


Fig. 15. Transmission electron micrographs of different aspects of similar polypropylene aggregates formed within nine hours of crystallizing the polymer from a 3/4% solution in amyl acetate at 115°C. (a) The aggregate is oriented with the plane of preferential development normal to the direction of viewing. (b) The aggregate is viewed parallel to the plane of preferential development. (x 30,200)

determine the exact lattice orientations within the constituent branches. The possibility that these aggregates are twinned dendrites is envisioned.

2.18 Kinetics of Spherulite Growth from Solution

G. M. Martin and E. Passaglia,

Polymer Physics Section

The rate of spherulite growth of polypropylene from a 2% solution in cis-decalin has been measured by dilatometric methods. The isotherms do not follow an Avrami law accurately, the deviations being in the direction expected by theory [F. Gornick and L. Mandelkern, J. Appl. Phys. 33, 907 (1962)]. However, the growth rate appears to be exponentially dependent on the reciprocal of the supercooling, as is customary.

Preliminary measurements indicate that the radial growth is not linear in time. This also is to be expected on the basis of theory.

2.19 Kinetics of Copolymer Crystallization

R. K. Eby,

Polymer Physics Section

There is quite a bit of evidence that some copolymers form lamellar crystals with the comonomer units incorporated within the lattice as point defects (Eby, 1964; also see Eby and Bolz, Technical Note 236, Section 5.13). One of the phenomena that this model must be able to account for is the fact that when a series of copolymers are cooled from the melt at about the same rate, the copolymers with a higher concentration of comonomer units form thinner lamellae [H. Hendue, *Ergeb. der Exakt. Naturwiss.*, 31, 363 (1959)]. While the explanation of this fact is straight-forward in a model based on exclusion of comonomer units from the crystal, it is not so obvious with the model presented above. We have approached this problem using the method of Hoffman and Lauritzen [J. Research NBS 65A, 297 (1961)], and taking account of the effect of the point defects on the various thermodynamic quantities involved (Eby, 1963). Initial results obtained with the simplest assumptions indicate a dependence of lamella thickness on point-defect concentration.

2.20 Theoretical Studies in Crystal-Whisker Growth

J. A. Simmons, R. E. Howard,
Metal Physics Section

R. L. Parker,
Crystallization of Metals Section

and

H. Oser,
Applied Mathematics Division

This work summarized in NBS Technical Note 236, Section 2.2 was presented at the Philadelphia meeting of the APS and is published (Simmons, Parker, and Howard, 1964).

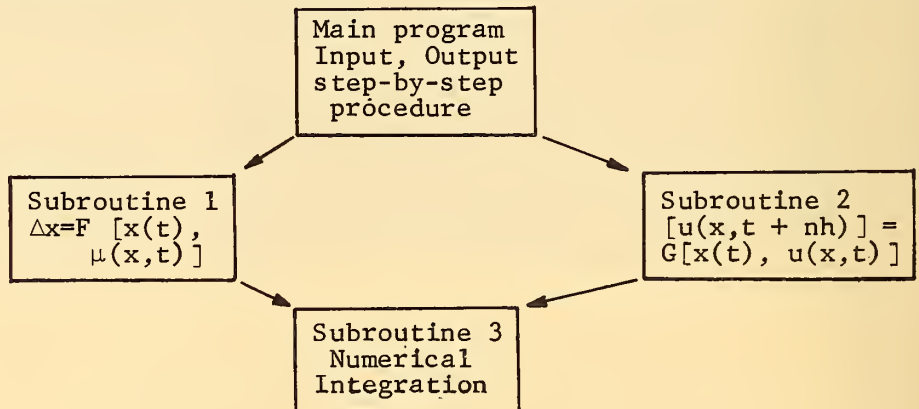
From the asymptotic formula for linear growth and the fact that $x(t)$ is always increasing the inequality

$$D \geq \frac{x^2}{\gamma} \left(1 + \frac{1}{\gamma T}\right)$$

permits lower bounds for the surface self-diffusion coefficient on close-packed planes to be computed from experimental data on whisker growth. Reasonable bounds were obtained by this method for 13 metals.

Results from the preliminary computer program mentioned in NBS Technical Note 197, Section 2.16, showed that a step-wise linear approximation to the growth curve was inadequate due to the extreme sensitivity of the concentration profile near the whisker tip to the rate of growth $x(t)$. This resulted in unstable numerical behavior of many of the integrals involved. Consequently, the computer program has been totally revised in order to obtain sufficient accuracy for both the whisker-growth curves and surface-concentration profiles.

The organization of the program is indicated in the following scheme:



Logical Organization of
Computer Program

The main program controls input and output of parameters and results, provides interpolation formulas for the effective evaluation of the integrals in the subroutines, and controls either the step-by-step computation of the growth increment Δx during the time step Δt or the concentration profile $u(x, t)$ by calling the appropriate subroutine 1 or 2 respectively. The third subroutine is an integration routine which records the numerical error of the result for control purposes. The increments Δx are computed in Subroutine 1 as follows:

$$\begin{aligned}
 \Delta X(t, nh) &= x(t+nh) - x(t) \\
 &= x(t) \left\{ e^{-\frac{nh}{\tau}} - 1 \right\} \\
 &\quad + \left(1 + \frac{1}{\tau}\right) nh \int_0^1 e^{-\frac{nh\lambda}{\tau}} x(t+nh(1-\lambda)) d\lambda \\
 &\quad + \frac{1}{2} nh \int_0^1 e^{-\frac{nh\lambda}{\tau}} \operatorname{erf} \left\{ \frac{x(t+nh) + x(t+nh(1-\lambda))}{\sqrt{nh\lambda}} \right\} \left[\dot{x}(t+nh(1-\lambda)) \right. \\
 &\quad \quad \left. - (x(t+nh) + x(t+nh(1-\lambda))) \right] d\lambda \\
 &\quad - \frac{nh}{2\sqrt{\pi}} \int_0^1 e^{-\frac{nh\lambda}{\tau}} \exp \left(-\frac{(x(t+nh) + x(t+nh(1-\lambda)))^2}{nh\lambda} \right) \sqrt{nh\lambda} d\lambda \\
 &\quad + \frac{1}{2} nh \int_0^1 e^{-\frac{nh\lambda}{\tau}} \operatorname{erf} \left\{ \frac{x(t+nh) - x(t+nh(1-\lambda))}{\sqrt{nh\lambda}} \right\} \left[\dot{x}(t+nh(1-\lambda)) \right. \\
 &\quad \quad \left. + (x(t+nh) - x(t+nh(1-\lambda))) \right] d\lambda \\
 &\quad + \frac{nh}{2\sqrt{\pi}} \int_0^1 e^{-\frac{nh\lambda}{\tau}} \exp \left\{ -\frac{(x(t+nh) - x(t+nh(1-\lambda)))^2}{nh\lambda} \right\} \sqrt{nh\lambda} d\lambda \\
 &\quad + \frac{1}{2} x(t) e^{-\frac{nh}{\tau}} \int_0^1 u(x(t)(1-\lambda), t) \left\{ \operatorname{erfc} \left(\frac{x(t+nh) - x(t)(1-\lambda)}{\sqrt{nh}} \right) \right. \\
 &\quad \quad \left. + \operatorname{erfc} \left(\frac{x(t+nh) + x(t)(1-\lambda)}{\sqrt{nh}} \right) \right\} d\lambda
 \end{aligned}$$

This equation arises from the conservation of mass and the implicit solution for $u(x, h)$ as a functional depending on the original concentration $u(x, 0)$ and the growth curve, $x(t)$ between the times $t=0$ and $t = nh$.

The computation of Δx permits a new interpolation approximation to $x(t)$ between $x(t + (n-1)h)$ and $x(t + nh)$. The interpolation maintains both $x(t)$ and $\dot{x}(t)$ continuous at all times. The new approximation for $x(t)$ between $t = 0$ and $t = nh$ is cycled back into Subroutine 1 for a still better approximation to the growth curve. Cycling is continued until a stated degree of accuracy is reached. A perturbation argument guarantees the convergence of this procedure for a finite time interval beyond $t = 0$.

Whenever the concentration profile is desired or when it becomes necessary to redetermine it for reasons of non-convergence of the Δx -iteration employed in Subroutine 1, Subroutine 2 is called to compute a new profile $u(x, t)$ and the iteration cycle begins anew. The expression for this concentration profile given by the above-mentioned functional is

$$\begin{aligned}
 u(\xi, t+nh) &= \frac{nh}{2} \int_0^1 e^{-\frac{nh\lambda}{T}} \operatorname{erf}\left(\frac{\xi + x(t+nh(1-\lambda))}{\sqrt{nh\lambda}}\right) d\lambda \\
 &\quad - \sqrt{\frac{nh}{\pi}} \int_0^1 e^{-\frac{nh\lambda}{T}} \exp\left(-\frac{[\xi + x(t+nh(1-\lambda))]^2}{nh\lambda}\right) \frac{\dot{x}(t+nh(1-\lambda))}{\sqrt{\lambda}} d\lambda \\
 &\quad + \frac{nh}{2} \int_0^1 e^{-\frac{nh\lambda}{T}} \operatorname{erf}\left(\frac{-\xi + x(t+nh(1-\lambda))}{\sqrt{nh\lambda}}\right) d\lambda \\
 &\quad - \sqrt{\frac{nh}{\pi}} \int_0^1 e^{-\frac{nh\lambda}{T}} \exp\left(-\frac{(-\xi + x(t+nh(1-\lambda)))^2}{nh\lambda}\right) \frac{\dot{x}(t+nh(1-\lambda))}{\sqrt{\lambda}} d\lambda \\
 &\quad + \frac{x(t)e^{-\frac{nh}{T}}}{\sqrt{nh\pi}} \int_0^1 u(x(t)(1-\lambda), t) \left[\exp\left(-\frac{(\xi - x(t)(1-\lambda))^2}{nh}\right) \right. \\
 &\quad \left. + \exp\left(-\frac{(\xi + x(t)(1-\lambda))^2}{nh}\right) \right] d\lambda
 \end{aligned}$$

Subroutine 3 is an integration procedure which records the truncation error for each integral. It is thus possible to control the step size automatically in order to keep the total error below a prescribed bound.

The computer program for this procedure has been written and is currently undergoing tests for its region of stability, the aim being to allow the computation of $x(t)$ on as coarse a grid $t + nh$ as possible in order to keep the computer use at a reasonable cost level.

3. DEFECT CHARACTERIZATION

This chapter is concerned with studies of defect-sensitive properties of single crystals.

3.1 Optical Properties, of "Pure" and Impure Crystals

R. F. Blunt,

Solid State Physics Section

The spectra of a number of systems have been measured, including "pure" ammonium chloride, NH_4Cl , and NH_4Cl doped with nickel, with cobalt, and with copper. Magnesium Fluoride, MgF_2 , has also been studied containing x-ray-induced color centers. Particular attention has been devoted to MgF_2 .

X-ray irradiated "pure" MgF_2 (rutile structure) produces, at room temperature, a strong band at ~ 250 nm (μ) (see report by M. I. Cohen, Section 3.2 of this Note). This band is easily bleached by 250 nm light, thereby producing a strong ~ 370 nm band. The ~ 250 nm band is slightly anisotropic, but the resulting bleaching appears completely independent of the orientation of the bleaching light. The 370 nm absorption band is markedly anisotropic, occurring only in $E \perp C$ spectra. Excitation with light of wavelengths of less than ~ 400 nm gives rise to two luminescent bands, one at 420 nm that occurs with $E \perp C$, and a band at ~ 550 nm that is isotropic. The luminescence is pronounced only when the exciting light has $E \perp C$.

Preliminary irradiation studies of samples at liquid-nitrogen temperature are currently in progress and so far have yielded weak thermoluminescence and evidence relatively weaker absorption bands than those obtained for room temperature irradiation. The absorption bands appear to be quite stable at room temperature, but are completely removed on a 500°C anneal.

3.2 Irradiation Studies

M. I. Cohen,

Solid State Physics Section

Work in connection with the study of color centers in crystals of magnesium fluoride, MgF_2 , has continued. During this period, several changes have been made in our equipment. A tungsten-target, high-output tube has been installed, increasing dosage rate by approximately four times. Arrangements have been made to irradiate crystals at low temperatures in an optical dewar that can then be transferred to a Cary 14 spectrometer without change in sample temperature.

As previously reported, (In Technical Note 236, Section 3.19), 50kV x-rays appear to be the most efficient radiation for production of color centers in MgF_2 . A number of samples of differing orientations and from different sources have been irradiated at varying dosage levels. Speci-

mens have also been irradiated and optically examined at 78°K. In addition to X-irradiation, a sample has been irradiated with 200 kV electrons (total exposure, $6 \times 10^6 R$). The results of these experiments are discussed by R. F. Blunt in Section 3.1 of this Note.

A sample of MgF_2 , obtained from Semi-Elements, Inc. was irradiated with 50 kV x rays for a total of three hours (total exposure, $\sim 10^7 R$). The sample was examined at intervals during the irradiation. The growth of the absorption band at 250 nm was found to be very rapid during the initial hour of irradiation. The growth rate of the absorption band then fell off rapidly with further irradiation.

3.3 Dislocation Studies in Metals

A. W. Ruff, Jr. and L. K. Ives,

Lattice Defects and Microstructure Section

The variation of stacking-fault energy with composition is being studied in a series of silver solid-solution alloys. The technique involves measurements on extended dislocation nodes observed by transmission-electron microscopy. Experiments involving silver alloys in the composition range 0 - 8 a/o tin are in progress. Preliminary results indicate that solute additions decrease the stacking-fault energy from that of pure silver and that extensive twin formation is observed at higher solute concentrations. The effects of compositional inhomogeneities (segregation to the faulted regions) will be examined, together with the effects of size and valence of different solutes. It is planned to compare the results with x-ray diffraction-faulting-probability measurements on the same alloy system. (see Section 3.4)

3.4 Stacking Fault Probabilities in Metals

C. J. Newton and A. W. Ruff, Jr.

Lattice Defects and Microstructures Section

A study of stacking-fault probability by means of x-ray diffraction effects has been undertaken in a series of silver alloys. Small relative changes in the separation of the diffraction peaks in the x-ray powder pattern are observed when one compares the pattern from the cold-worked material with that from annealed material of the same composition. This relative peak shift, as well as certain other diffraction effects, enables one to calculate the probability of faulting in the cold-worked material. The specimens examined at present are carefully prepared from filings of the alloys; consideration is being given to measurements on solid-alloy specimens with a fine grain structure. (see Section 3.3)

3.5 Thermodynamics of Segregation of Solute Atoms to Stacking Faults in FCC Binary Alloys

R. deWit,
Lattice Defects and Microstructure Section

and

R. E. Howard,
Metal Physics Section

Since the stacking-fault energy in many FCC (face-centered cubic) metals is lowered by alloying, thermodynamic equilibrium requires that some segregation of solute atoms to the stacking faults takes place to lower the total free energy. Instead of assuming with others that the width of the extended dislocations remains fixed during the segregation, we suppose that the width always has the equilibrium value corresponding to the local concentration at the stacking fault and thus changes continually. A further generalization that may be more realistic was also made, which was not previously considered (see NBS Technical Note 236, Section 2.3). Instead of maintaining mechanical equilibrium for the extended dislocations, no such "a priori" assumption was made. Now, two general conditions of thermodynamic equilibrium are found. The first is the same as that derived previously without the above assumption by Dorn and Suzuki; it gives the relation between the solute concentration X^f in the faulted region and X in the matrix if the stacking-fault energy dependence on the local concentration is known, and can be interpreted as a Maxwell-Boltzmann distribution of the solute. The second is a new expression for the stacking-fault width w in terms of the stacking-fault energy and an entropic term, and can be interpreted in terms of the balance of forces on each partial dislocation.

It is found that the locking stress, which is the resolved shear stress required to free a dislocation from its segregated atmosphere, is not changed by the above extension of the theory.

On the crude approximation that the stacking fault energy γ is exactly the difference in the free energy of the FCC and HCP (hexagonal close-packed) structures of the same composition and temperature, it is shown that the FCC and HCP phase boundary concentrations of the alloy are found as a special case of the theory when the stacking fault width approaches infinity. This shows again, contrary to Suzuki, that the stacking fault width cannot increase indefinitely.

The stacking fault energy versus composition dependence for the unsegregated alloy is given by the γ versus X^f curve; for the fully segregated alloy this dependence is given by the γ versus X curve. Both the γ versus X and the w versus X curves are found from the γ versus X^f curve by the two conditions of equilibrium. It is suggested that work-hardening experiments may measure the γ versus X^f dependence, dislocation node measurements the w versus X dependence, and x-ray experiments the X^f versus X dependence.

The present theory may have important applications to the measurement of the stacking-fault energy which is an important parameter in theories of mechanical properties of materials.

3.6 Characterization of Electrodeposited Crystals

F. Ogburn and A. de Koranyi,

Electrolysis and Metal Deposition Section

Examination of electrodeposited lead dendrites, which are flat or 2-dimensional, shows them to be oriented with $\{111\}$ planes parallel to the plane of the dendrite. At least two orientations with a twist relation about the common $\{111\}$ pole are always present. The twist angles observed were 20° , 27° , 30° , 33° , 37° , and 50° . For each dendrite, the direction of growth was half way between a $[211]$ direction of one orientation and a neighboring $[211]$ direction of the other orientation.

Another phase of this project involves development of techniques for growing copper dendrites by electrodeposition in such a size and form that they may readily be used for other experiments. This empirical study has been informative, but only partially successful in that controlled growth of a single dendrite has not been achieved. Several of the dendrites, the dimensions of which are measured in millimeters and centimeters, were examined metallographically. The twinned structure reported in Technical Note 236, Section 3.10 was consistently observed. Not infrequently, however, other structures were observed along with the twin boundaries. It remains to be determined if this structure is inherent and what it is due to.

3.7 Defects in Thin Oxide Films

J. Kruger and C. L. Foley,

Corrosion Section

Thin-foil electron microscopy and diffraction were applied to a study of the films formed on iron during potentiostatic anodic polarization. The techniques consisted of anodically polarizing thinned iron-foils in boric acid-sodium borate solutions at various passive potentials. By then flooding the surface, while it was at the passive potential with an inert liquid it was possible to retain the electrochemically formed films so that they could be studied in the electron microscope. Selected-area transmission electron-diffraction studies of these foils offered the advantage that one could study the epitaxial relationship of the oxide with metal substrates of different orientation on a single polycrystalline specimen.

These studies have shown that the films formed under the above described conditions are highly oriented, and have a spinel structure. The major difference between the passive and non-passive films was found to be the appearance of superlattice lines in the case of the passive films. These lines are those predicted by Bloom for $\gamma\text{-Fe}_2\text{O}_3$ containing hydrogen in vacant iron sites. This work (Kruger and Foley, 1964) will be presented before the Electrochemical Society in October.

L. H. Bennett and R. W. Mebs,

Alloys Physics Section

The interaction of the nuclear-electric-quadrupole moment with crystal lattice-vibrations is the mechanism which makes possible the detection of nuclear magnetic resonance in bulk materials by the acoustic excitation method. This type of investigation suggests itself as being particularly useful in the study of the nuclear magnetic resonance in metals, since it permits the employment of single crystals instead of finely divided metallic powders usually employed in conventional nuclear magnetic resonance studies.

The crystals employed are those with limited numbers of structural defects such as dislocations, vacancies and stacking faults, and it must be possible to provide optically flat and parallel faces to each sample without appreciably disturbing its defect structure. Inasmuch as the metals selected must have a large quadrupole moment, the investigation further lends itself to a study of the effect of its defect character, as well as a quantitative measurement of the quadrupole interaction. Furthermore, the influence of the orientation of the applied magnetic-field with respect to the crystalline axes on the intensity of the measured resonance can be studied inasmuch as some defects have a directional preference with relation to such axes.

The present investigation is employing a nuclear-resonance spectrometer system consisting of an oscillator-detector-recorder assembly plus an adjustable high-intensity precision electromagnet with a centrally homogeneous field. Some additional matching circuitry is used with the transducer-crystal probe, and has been used successfully in observing nuclear-magnetic acoustic resonance in a potassium-iodide single crystal.

Additionally, high-purity copper and indium antimonide single crystals have been secured, the latter possessing a fairly low carrier concentration. Although suitable barium-titanate transducers have been obtained for use with the copper sample, to date no reproducible measurable resonance has been detected. There was a preliminary unsatisfactory attempt to measure resonance with the indium antimonide crystal with attached quartz-crystal transducer. Subsequently, normal nuclear magnetic-resonance measurements were made with the same spectrometer on this crystal, with its axis being rotated with respect to the magnetic field. No measurable variation of resonance amplitude with respect to orientation could be detected. This might indicate either that the crystal was quite free of defects, or that the deformation had extended beyond the point where only preferential planes were involved. Hence, the crystal was carefully strain-relief annealed in hydrogen and again prepared for test.

A broad survey is being made of available single crystals of metals possessing suitable quadrupole moments, both from industrial sources and from our own single-crystal facilities. Such crystals necessarily must be of high purity and possess a limited number of defects.

3.9 Laser Microprobe for Analysis of Very Small Samples

B. F. Scribner, M. Margoshes,

and

S. D. Rasberry,

Spectrochemical Analysis Section

A description of a laser microprobe source for analysis of small samples was given in NBS Technical Note 197, Section 3.10. In the last six months, experiments with this apparatus have been directed toward improving the reproducibility of this source, and investigating the character of sample vaporization by the laser and the sparking of this vapor with cross-electrodes.

Apparatus was designed to detect the laser-power output as a function of time, simultaneous with sample volatilization by the laser. This direct observation of the laser permits immediate evaluation of changes that variations in laser optics and pumping made in the laser output, and size of pit produced on the specimen. Modifications were made to bring the giant-pulse ruby laser into single-spike operation, resulting in better reproducibility of laser operation, and sample vaporization. The modifications required to achieve reproducible single-spike operation were: Use of a more angle-selective front reflector, partial internal masking of the laser cavity, and lowering operating temperatures by 25 °F and 80 °F. The difference in power output, as a function of time, between multiple-spike and single-spike operation is illustrated in Figure 16. The variation of crater diameter with an increase in laser energy output for single-spike operation is illustrated in Figure 17, where the sample is NBS Zn Base Standard 629.

The more consistent laser output available with the single-spike laser pulse permits greater confidence in studies of other variations in the system. The characteristics of sample excitation, as a function of spark voltage, resistance, capacitance, inductance, and electrode configuration have been determined in the case of varying these parameters singly. Results indicate that the intensity changes which accompany variations in these source parameters differ between the laser microprobe-spark and conventional spark sources. This difference may be accountable to the fact that in conventional spark sources the spark volatilizes as well as excites the sample.

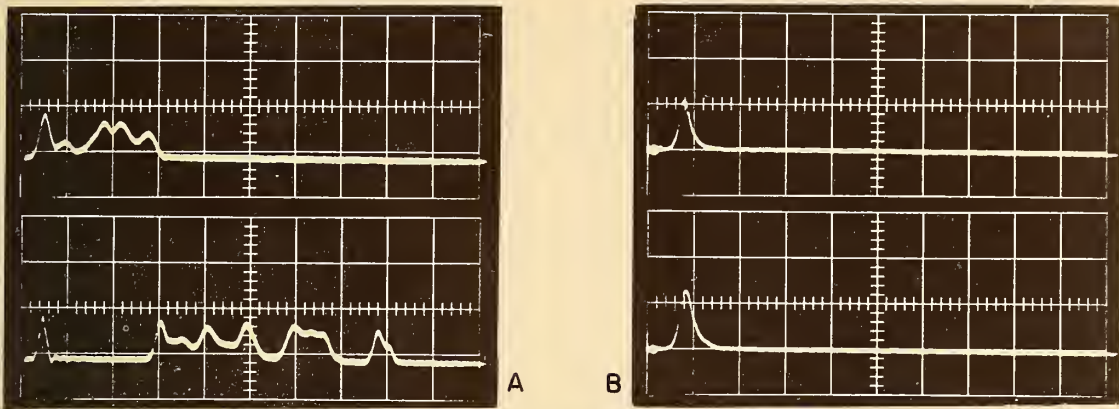


Fig. 16. Recordings of power vs time for (a) multiple-spike laser output and (b) single spike laser output. Two successive recordings are shown for each case. Time scale; 200 nanoseconds= 1 large division.

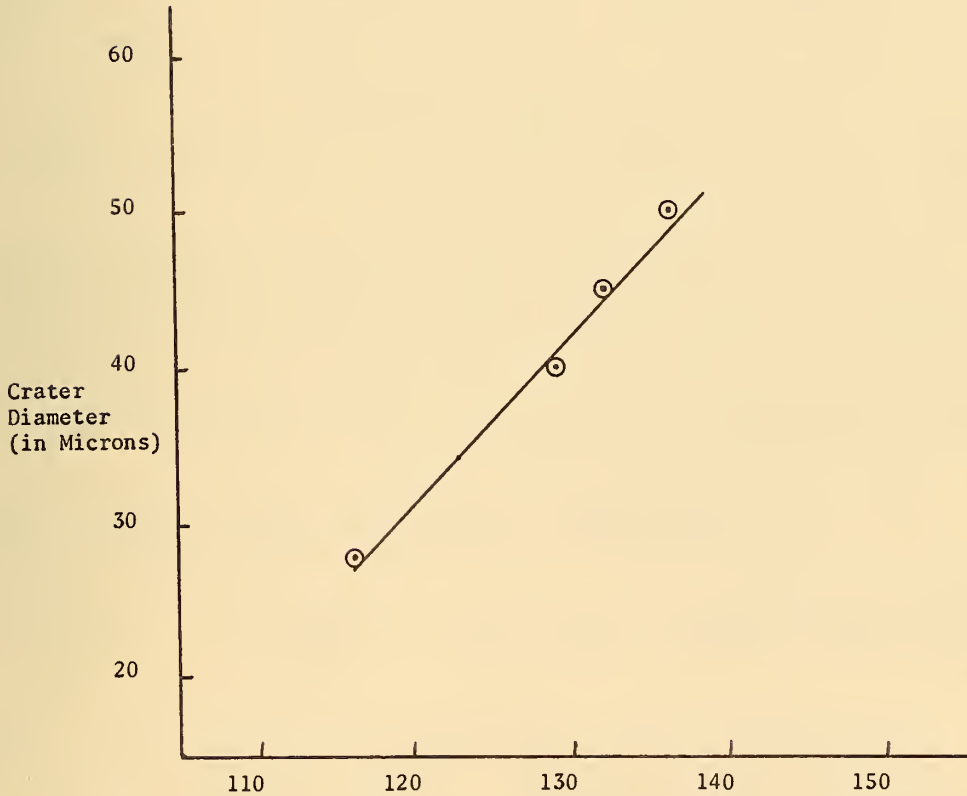


Fig. 17. Crater diameter vs laser output. Sample is NBS Zn base Standard 629.

3.10 Accurate Measurement of the Fundamental Electrical Properties of Semiconductor Crystals

J. C. French, L. J. Swartzendruber,
G. G. Harman, H. A. Schafft,

and

N. Winogradoff,
Electron Devices Section

Following the completion of the solution of a number of electrical potential problems having application to two- and four-point probe measurements, as described in NBS Technical Note 236, Section 3.12, the remaining results were prepared for publication (Reber, 1964) (Swartzendruber, 1964a, b, and c). Some of this material will be a part of the American Society for Testing and Materials Proposed Tentative Method of Test for Silicon Radial Variation of Resistivity, which is now in draft form.

Attention turned to the experimental determination of the resistivity variation in silicon single-crystals. This variation appears to be one of the limiting factors in the establishment of standard samples. The best commercial sample received for evaluation varied in resistivity (about a nominal value of 14 ohm cm) by $\pm 4\%$ over a diameter of 3.3 cm and $\pm 5\%$ over a length of 2.5 cm. A neutron-irradiated sample of about the same resistivity was not greatly superior to this. Unfortunately, these variations are not monotonic functions of distance so that correction for their effect is difficult. A cooperative program with industry has been established with the aim of producing more uniform material specifically for this purpose.

A thorough study of the accuracy attained to date in the resistivity measurements was completed. Measurements were made on both circular wafers and rectangular parallelepiped bars cut from the wafers, using both two- and four-point probe techniques with two different probe spacings. Appropriate allowance was made for anticipated errors arising from the effects of the many factors involved, such as sample dimension variation, probe spacing variation and misplacement of the probes, and temperature effects, after these factors had received both experimental and theoretical analysis.

In the case of this 14 ohm-cm material, and on a single laboratory basis, the various measurements were found to have one sigma (standard deviation) limits of error of less than one-half percent, and the various measurement methods agreed to within this experimental error. Further work to improve these results is underway. It is expected that the limit of error will be reduced in any event on the one ohm-cm standard sample currently of greatest interest.

A new task has been undertaken in the study of second breakdown in transistors* mentioned in NBS Technical Note 236, Section 3.12. This is a cooperative effort with industry, concerned with determining the importance to the development of second breakdown of strain, dislocations and other irregularities in the single-crystal semiconductor, in the transistor. X-ray diffraction microscopy will be used to observe these defects and a correlation of the defect sites with preferred

* This work was supported by the Rome Air Development Center.

locations of second breakdown will be sought in specially constructed transistors.

Work was started on a new program in which the recombination properties of hot carriers in silicon crystals will be studied. A literature survey and a band structure study were made, program objectives were established, and instrumentation was completed.

Some additional results have been published which have arisen from the now concluded studies of muscovite mica (Ruthberg and Frankel, 1964).*

The solid-state technology project has continued to devote most of its effort to work on silicon-crystal nuclear-particle detectors. However, its sample preparation and analysis facilities have also contributed to the crystal characterization by diffraction topography of R. D. Deslattes in locating material of suitable dislocation density, in preparing this material for x-ray analysis, and in correlation of chemical methods of dislocation density with x-ray methods.

Study of solid-state injection lasers began in the last weeks of June, 1964.

3.11 Study of Crystal Defects

D. J. Barber and N. J. Tighe,

Physical Properties Section

The motion of dislocations in aluminum oxide at ~ 1500 °C has been observed directly, using the high-temperature electron microscope stage reported previously in NBS Technical Note 236, Section 3.4. The results indicate that, at these temperatures, the passage of 100 kv electrons through the sample produces point-defects. The defects subsequently interact with dislocations, causing them to climb in a characteristic way, resulting in a zig-zagged appearance (Figure 18).

The hot stage has also been used to study phase transformation in single crystals of quartz. During this work, the existence of extended stacking faults on the $\{1011\}$ planes has been revealed (Figure 19). The faults are unaffected by the transformation at 573 °C from the α - to the β - quartz structure. Further study of the transformations is to be carried out using a ciné-camera.

* This work was supported in part by the General Services Administration.

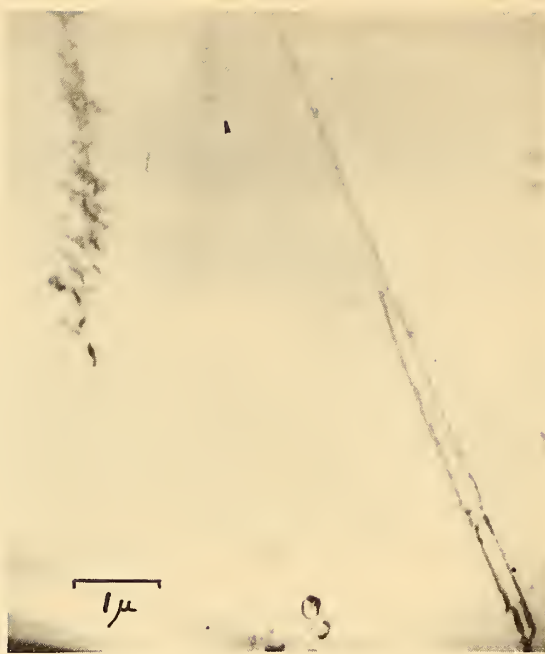


Fig. 18. Stacking fault in (0001) section of α -quartz prepared by chemical thinning.



Fig. 19. Climbing dislocations in α -Al₂O₃ under the influence of a flux of point defects at $\sim 1500^\circ\text{C}$.

L. M. Matarrese, J. S. Wells, R. L. Peterson,
R. J. Mahler, and A. R. Cook,

Radio and Microwave Materials Section

The analysis of the EPR spectrum of ferric ion in quartz has been completed. The work was reported at the APS meeting in Washington, and a paper is being prepared for publication. The values of the spin Hamiltonian parameters that fit the data best are D (assumed positive) = 734, 1 G, $E = 327.7$ G, $a_0 = 37, 5$ G, and g (isotropic) = 2.0043.

We plan to extend the investigation of iron-doped quartz to low temperatures and zero field. (The zero-field splittings calculated from the above parameters are approximately 6,6 and 8,5 GHz); see Figure 20, 21, and 22.

We believe that the ferric ions are in substitutional sites, and that a small positive ion, such as Na^+ , Li^+ , or H^+ on the two-fold axis and in the open optic-axis channel provides the charge compensation and the strong axial field. ENDOR experiments are planned in an attempt to check this hypothesis.

The EPR spectrum of amethyst has also been attributed to ferric ion but is completely different from that of our iron-doped quartz specimens.

Another K-band EPR spectrometer has been assembled for use in AFMR experiments on the anhydrous sulfates of transition metals, which have relatively low Néel temperatures. Preliminary experiments on powdered anhydrous CuSO_4 show that there is still a paramagnetic resonance signal below the Néel point (34 °K). This may be due to an impurity. We are now investigating single crystals of CuSO_4 .

We have continued studies of the ultrasonic modulation of the magnetic interaction in antiferromagnetic KMnF_3 . Results have been published in Physical Review Letters (Denison, James, Curran, Tanttliia, and Mahler, 1964) and will also be presented at the 13th Colloque Ampère. Attempts to detect this effect in antiferromagnetic $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and RbMnF_3 , and in paramagnetic LiF , ZnF_2 , and ruby met with failure. We are now trying to observe a Raman phonon-doubling process in RbMnF_3 and KMnF_3 .

ROTATION ABOUT Z AXIS

— site 1, --- site 2,
 - - - site 3, ψ 1,2,3 constant

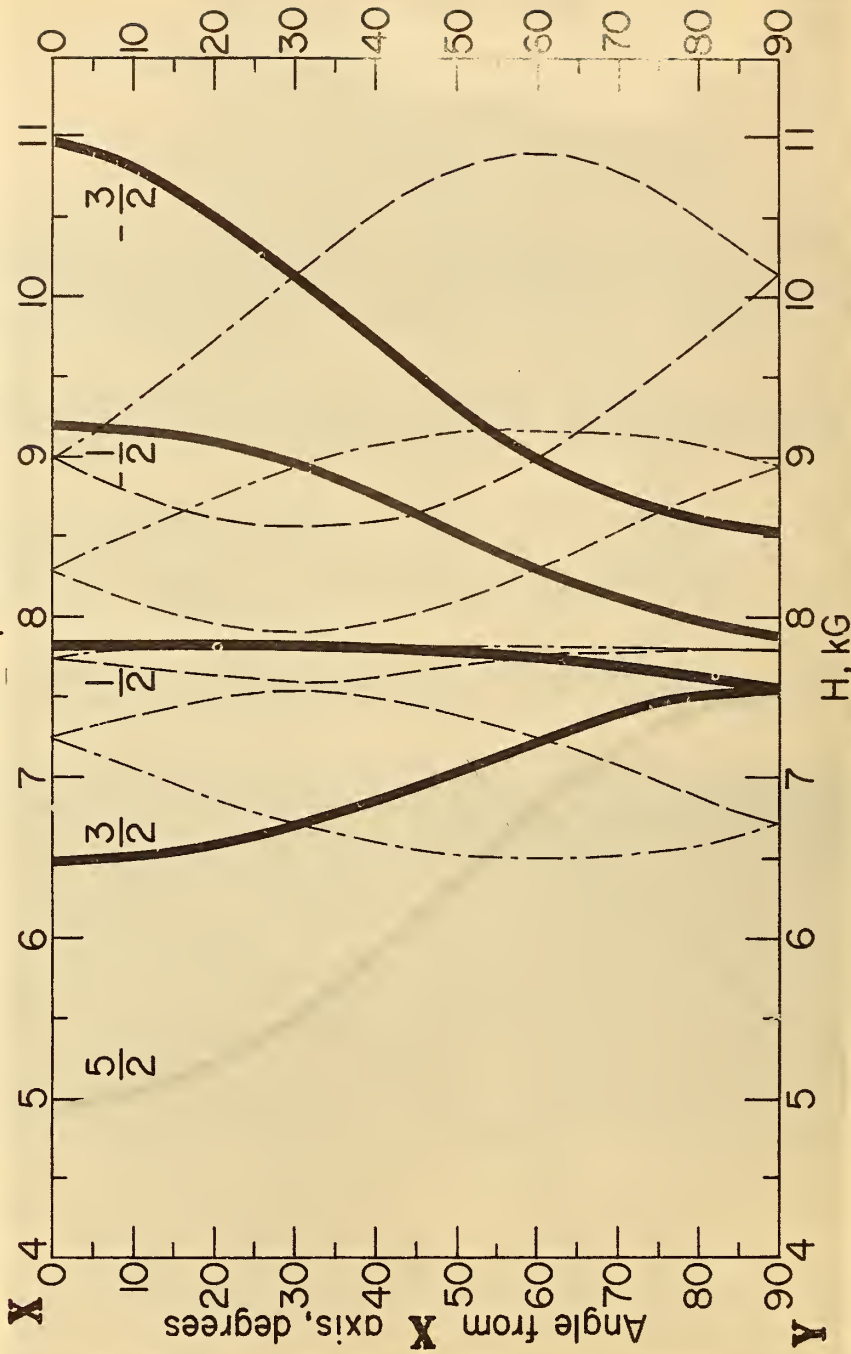


Fig. 20. Angular dependence of the EPR lines from Fe^{3+} in quartz in rotation about the Z axis (the optical axis) of quartz. Note the repetition of the spectral pattern every 60° . This implies that the three sites are on the three two-fold axis of quartz, which are 120° apart in the rotation plane.

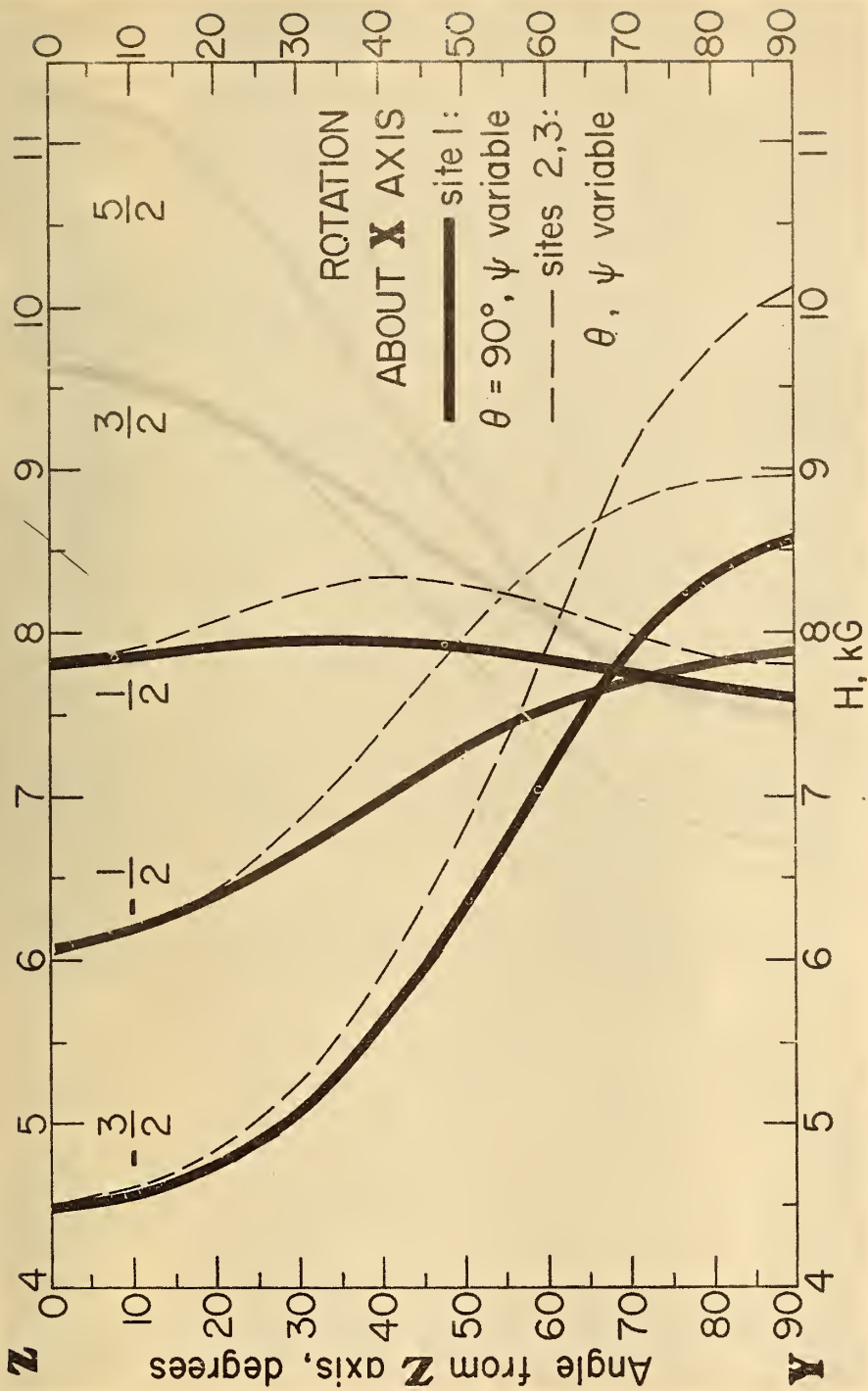


Fig. 21. Angular dependence of the EPR lines from Fe^{3+} in quartz in rotation about an X axis (one of the two-fold axes) of quartz. Note that all three sites are equivalent when the field is parallel to Z and that sites 2 and 3 are equivalent in this plane.

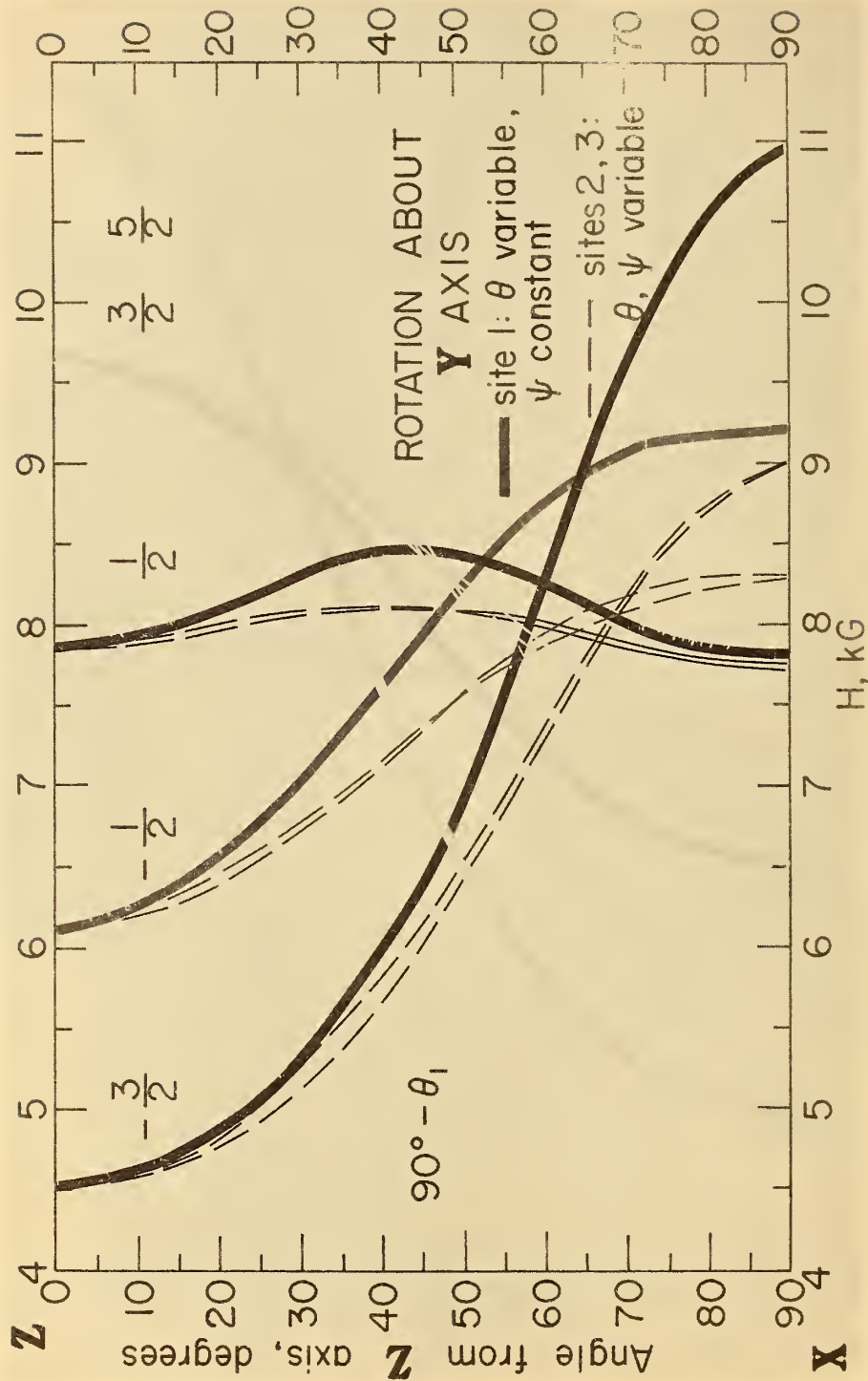


Fig. 22. Angular dependence of the EPR lines from Fe^{3+} in quartz in rotation about a Y axis (perpendicular to a two-fold axis and the optical axis) of quartz. Note that sites 2 and 3 are not quite equivalent in this rotation plane. This is due to the complex nature of the rhombic field.

3.13 Effect of Point Defects on the Dynamic Properties of Crystals

J. B. Wachtman, Jr., S. Spinner,

and

S. Marzullo,
Physical Properties Section

Mechanical 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.

Previous work on vacuum reduced rutile (Wachtman and Doyle, 1964) and on Ni-doped rutile has been extended both by combining the effects of vacuum reduction and Ni doping and by Cr doping. Results appear to be consistent with the idea that in all cases interstitial metal ions are present and that the measured activation energies are those for ionic jumps between interstitial sites. In the case of Ni-doped rutile, two peaks appear which have been attributed to paired and unpaired interstitials, respectively. This interpretation is supported by the observation that the peak associated with pairs is still present after vacuum reduction, but the peak attributed to isolated Ni interstitials vanishes presumably because of association of these Ni ions with interstitial Ti ions introduced by vacuum reduction.

Work on the dielectric loss peak associated with small amounts of CaO in solid solution in ThO₂ has been continued. The size of this peak increases with increasing CaO content up to one mole percent, but thereafter remains unchanged up to 10 mole percent, despite the fact that as much as 12.5 percent CaO will go into solid solution. The internal friction peak associated with CaO in ThO₂ shows the same behavior.

3.14 Crystal Characterization by Double Crystal X-ray Diffraction Topography

R. D. Deslattes and B. Paretzkin,

Crystal Chemistry Section

The work described previously (NBS Technical Note 236, Section 3.13) has been continued, especially on solution-grown ADP (NH₄H₂PO₄). With careful sample preparation and handling, specimens have been obtained whose topographs show neither local defect images nor significant strain over regions exceeding 1 cm² (Deslattes et al., 1964).

The perfection of these crystals together with the existence of rather numerous strong reflections provide a significant series of perfect reference specimens with which this technique can be extended to many other crystals.

Another application of these crystals is in high resolution x-ray spectroscopy. Of the reflections so far studied, the following results

have been obtained in the double-crystal spectrometer at the wavelength of CuK_α (1.54Å).

<u>Reflection</u>	<u>Resolving Power</u> ($\frac{\lambda}{\Delta\lambda}$)
202	4.0×10^4
220	4.5×10^4
600	4.5×10^5

The 220 reflection is of particular merit since it is unaccompanied by other orders and has a percent reflection of 60.

3.15 Magnetic-Resonance Studies - I

T. Chang, R. A. Forman,

and

R. C. Frisch,
Solid State Physics Section

The work of this group can be broken into two main categories, nuclear magnetic resonance and electron paramagnetic resonance. Certain materials are being investigated by both methods; for example, ammonium chloride, NH_4Cl , rutile, TiO_2 , and strontium titanate, SrTiO_3 , while several others are specific to just one method.

(a) Electron-Spin Resonance

Electron paramagnetic resonance studies of transition metal-ion impurities in rutile are continuing. Earlier work on molybdenum, Mo^{5+} , in rutile has been completed and work is in progress on tungsten, W^{5+} , in rutile. Both of these ions enter the rutile lattice substitutionally and both have a d^1 electron configuration in the valence states studied. This is the first observation of tungsten as an impurity in a crystalline lattice.

Since superhyperfine structure of the resonance line, which is the effect of the interaction of the impurity electrons with neighboring titanium nuclei, is observed for both Mo^{5+} and W^{5+} in rutile, a correlation of the two results was suggested. This correlation is possible because both have similar (d^1) electronic configurations and the same crystalline environment.

In addition to the above, work has begun on transition metal impurities in ammonium chloride and strontium titanate. Some work has also been begun to aid in the identification of the color center (s) produced by x-ray irradiation of MgF_2 being studied by Blunt et al (see Section 3.1).

(b) Nuclear Resonance

The nuclear magnetic resonance study of potassium azide, KN_3 , has been completed and the quadrupole coupling-tensors for all nitrogen sites in the crystal have been determined. The relatively small size of the

quadrupole coupling constants has necessitated the construction of new apparatus for searching for the pure quadrupole resonance in other azides where a nuclear magnetic resonance study is not feasible. Searches for resonances in sodium azide will be begun shortly.

Preliminary measurements have also been made on the N^{14} nuclear resonance in single crystals of ammonium chloride. A temperature dependence study is currently in progress. Ammonium bromide and iodide will also be investigated if large enough single-crystals can be grown.

Measurements of linewidths and chemical shifts of nitrous oxide, N_2O , nitric oxide, NO , nitrogen trioxide, N_2O_3 , and nitrogen dioxide, NO_2 , are also in progress. These measurements will be useful for estimating quadrupole effects to be expected for the nitrate and nitrite ions in crystals. Single crystals of sodium nitrite, $NaNO_2$, and sodium nitrate, $NaNO_3$, have been prepared, and searches are being conducted for the nitrogen resonance in these materials.

Helium temperature investigations of rutile and strontium titanate are planned. The quadrupole interactions of the titanium nucleus are presently unknown.

3.16 Automation of Single-Crystal X-Ray Diffraction Intensity Measurements

F. A. Mauer,

Crystallography Section

Plans for the automation of an existing diffractometer and single-crystal orienter were discussed in NBS Technical Note 236, Section 3.14. The prototype system has been assembled and is under test by the manufacturer. If its performance is satisfactory, the National Bureau of Standards is to receive the first production models of the programming and positioning modules. Installation is expected by January 1, 1965.

4. PHYSICAL PROPERTIES OF CRYSTALLINE MATERIAL

This chapter is concerned with the physical properties of crystalline material where crystal perfection is not a primary consideration.

4.1 Crystal Orientation Methods*

E. N. Farabaugh and P. R. Miller,

Crystal Chemistry Section

A study of the standard x-ray orientation procedures for single

* This work is partially supported by the Atomic Energy Commission

crystals has been undertaken to determine in what way these procedures can be modified or refined to obtain the orientation of a crystal more quickly and precisely. Laue back-reflection photographs and pseudo-Kossel line patterns are used in the program. The techniques developed will be applied in support of other crystal research in which the orientation of the individual crystal is a necessary part of the investigation.

4.2 Crystal Symmetry and Crystal Properties

J. B. Wachtman, Jr.,
Physical Properties Section

and

H. S. Peiser,
Crystal Chemistry Section

The application of stress to a crystal causes a lowering of symmetry in general with the result that atoms which originally had the same energy levels may become non-equivalent and have different energy levels. This non-equivalence affects many properties such as internal friction, optical spectra, electron spin resonance, etc., which are associated with the atom in question. Quantitative treatment of these effects requires a detailed theory for each, but selection rules can sometimes be derived from symmetry considerations alone (compare NBS Technical Note 236, Section 3.7). For this purpose, it would be useful to have a tabulation of the possible patterns of non-equivalence which can be set up by any possible stress for all types of positions in each of the 230 crystallographic space groups. This large task can be somewhat reduced by tabulating only the general position for each space group because the special positions can then be derived easily. This tabulation has now been completed for the centro-symmetric space groups and work is in progress on the noncentro-symmetric space groups.

4.3 Studies in Solid-State Theory

A. H. Kahn,

Solid State Physics Section

A study of the electronic-energy bands of cuprous oxide has been started. The tight-binding method is being applied in the same way as in the recently completed study on strontium titanate, SrTiO_3 .

Comparison with experimental transport and optical properties will be made.

Published experimental infrared reflection data were analyzed to obtain information about the long-wavelength polar modes of lattice vibration in rutile, TiO_2 . The continuum polarization model of electron-phonon interactions was extended to apply to crystals with several types of longitudinal polar phonons, and the results were used to discuss polaron theory in rutile.

4.4 Electronic Transport

H. P. R. Frederikse, J. H. Becker, W. R. Hosler,
R. C. Keezer, D. E. Poland*, W. R. Thurber,

and

A. Mante**
Solid State Physics Section

Experimental determinations of the energy-band structure of strontium titanate, SrTiO_3 , (see NBS Technical Note 236, Section 4.4) are continuing through measurements of the Hall coefficient, electrical conductivity, thermoelectric power, and recently the orientation dependence of magnetoresistance. Preliminary results on magnetoresistance at 4.2 °K are consistent with the calculations previously made (Kahn and Leyendecker, 1964). Studies will be extended to include piezoresistance. Improvements have been made in the preparation of crystals with specific electron concentrations (oxygen deficiencies). These specially prepared crystals are also being used in connection with research on superconducting semiconductors (see Research on Superconducting Semiconductors, Section 4.21 of this Note).

In connection with the superconductivity and energy band structure determinations, several other materials are being investigated. These include BaTiO_3 , MoO_3 , Na_xWO_3 , AuSb_2 , several II-VI and IV-VI compounds (see Section 2.10).

Facilities are being assembled and tested for studies of tunnelling between metals and insulators (or semiconductors) which will yield information concerning electron and phonon energy spectra.

The apparatus for studies of thermal conductivity at low temperatures has been improved and used in connection with studies of rutile. Umklapp processes determine the temperature dependence of the thermal conductivity in the range 25-300 °K. The value in the c direction is 1.5 times that in an a direction above 15 °K. These samples of pure TiO_2 have now been reduced to determine the effect of lattice defects on the thermal conductivity.

4.5 Optical Constants of Materials from 1 to 1000 Rydbergs

R. E. LaVilla and R. S. Deslattes,

Crystal Chemistry Section

This is a new project whose objects are (a) to extend and improve knowledge of optical constants of materials, (b) to extend the techniques of good crystal spectroscopy into the region where it overlaps

* NAS-NRS Research Associate

** NATO Fellow

with good ruled grating spectroscopy and (c) to undertake on the little understood and presently controversial subject of the extended fine-structure in the x-ray absorption-edge spectra of materials. This would involve studies from 1 to 1000 Rydbergs ($\lambda = 1000\text{\AA}$ to 1\AA).

The numerical procedures have been tested for extending and improving the data in the spectral region up to 3 Rydbergs. We plan to extend these techniques to shorter wavelengths. Also, we will procure and assemble a single-crystal vacuum spectrometer for absorption measurements in the 20 - 200 \AA range on extremely pure materials.

4.6 Hall-Effect Measurements*

S. Rubin,

Engineering Electronics Section

The objective of this project, as indicated in NBS Technical Note 236, Section 4.5, is the establishment of standardized terminology and measuring methods for galvanomagnetic (Hall effect and magnetoresistive) devices.

The results of the work of this project on sensitivity indices for Hall generators have been published (Rubin and Rogers, 1964) and, in addition, two other papers have been issued which present a tutorial introduction to galvanomagnetic effects and describe proposed standards for Hall generators (Rubin, 1964).

Work on standards of terminology and measuring methods for magnetoresistors and galvanomagnetic multipliers is continuing, and it is anticipated that proposed standards in these areas will be available by the middle of calendar year 1965.

4.7 Dielectric and Mechanical Properties**

J. H. Wasilik,

Solid State Physics Section

We have applied the Nath, Born-Smith de Launay theory for diamond lattices [de Launay, Solid State Physics, 2, 219 (1956)] to several

* This work was supported by the Bureau of Naval Weapons

** This work was supported by the Atomic Energy Commission

zinc-blende structures. By a simple modification, we have reduced the number of independent atomic-force constants from three to two, while still retaining interaction out to next-nearest neighbors. Assuming the interaction energies of the ions are describable by a Born-Mayer potential, $V = -Ae/4 + B \exp(-r/p)$, we show that the next-nearest neighbor, central-force force constant (de Launay's α_2) is equal to the nearest-neighbor, central-force force constant (de Launay's α_1) times (nearest-neighbor distance/next-nearest-neighbor distance)³. This reduction of the number of independent force constants results in a relationship among the three elastic constants which can be conveniently expressed as $C_{44} = f(C_{11}, C_{12})$. The calculated values of C_{44} are given in Column 2 of Table I, and are compared with the experimental values, Column 3.

Using an expression given by de Launay (op. cit. p. 294) and our relationship between α_1 and α_2 , we have calculated the transverse optical mode frequencies, Column 4; the experimental values are given in Column 5. In this calculation our relationship is not a necessity, but it simplifies the computation and constitutes a further test for our assumption.

Also, using a straightforward Clausius-Mosotti, Lorenz-Lorentz approach, we have obtained the lattice polarizability which is equated to an effective charge/atomic-force constant, the same atomic-force constant being used as in the transverse-optical-mode calculation. We then calculate the effective lattice charge using as input data the high-and low-frequency dielectric constants and the elastic constants. The results are given in Column 6 of the table and are compared with other results in the literature, Columns 7, 8, and 9.

TABLE I

1	2	3	4	5	6	7	8	9
	C_{44}	C_{44}	ω_{TO}	ω_{TO}	e^*	e^*	e^*	e^*
Material	calc.	exptl.	calc.	Picus	calc.	Picus	Whelan	Fan
	$\times 10^{11}$ dynes/cm ²		$\times 10^{13}$	sec ⁻¹		et al.	in	Hannay
InSb	3.034	3.018	3.11	3.28	.332	.34	.34	.34
GaSb	4.56	4.325	4.18	4.25	.267	.30	.18	
AlSb	4.38	4.15	5.87	5.92				
InAs	3.77	3.959	3.74	3.95				
GaAs	6.16	5.94	5.09	5.04	.418	.43		.46
CdTe	1.56	1.994						

4.8 Electron-Spin Resonance of Transition-Metal Complex

H. C. Allen, Jr. and G. F. Kokoszka,

Inorganic Materials Division

The electron-paramagnetic-resonance of monomeric cupric ions in zinc-doped copper acetate monohydrate has been observed at 77 °C, using

an X-band spectrometer. Single crystals containing less than 1% zinc ions were grown from a slightly acidic aqueous solution containing about 75% copper acetate and 25% zinc acetate.

The experimental results could be fitted to the spin Hamiltonian $H_s = g_z \beta H_z S_z + g_x \beta H_x S_x + g_y \beta H_y S_y + A_z S_z I_z + A_x S_x I_x + A_y S_y I_y$. The values $A_z = 0.0147 \pm .006 \text{ cm}^{-1}$, $A_x < 0.0018 \text{ cm}^{-1}$, and $A_y < .0023 \text{ cm}^{-1}$ were measured for the monomeric cupric ions. The g values were found to be $g_z = 2.344 \pm 0.005$, $g_x = 2.052 \pm 0.007$, and $g_y = 2.032 \pm 0.007$.

These results are consistent with a model proposed by Slichter [Phys. Rev., 99, 479 (1955)] in which he has shown that the components of the hyperfine tensor should be twice as large for a monomeric species as compared to the dimeric species when the exchange integral, J , is much larger than the components of the hyperfine tensor. The g values are expected to be the same for the monomeric and dimeric species. A comparison of our results with the results of Bleaney and Bowers [Proc. Roy. Soc. (London) A214, 451 (1952)] and Abe and Shimudu [Phys. Rev., 90, 316 (1953)] shows a satisfactory agreement of experiment and theory.

Recently, we have reported on the electron-spin-resonance of some tris couples of copper [Allen, Kokoszka, and Inskeep, (1963)]. The magnetic parameters were obtained from polycrystalline samples of the copper complex in the corresponding zinc matrix. It now has been possible to grow single crystals of the tris coordination compound of Zn^{+2} with 1-10 phenanthroline containing a small amount of the corresponding cupric complex. The magnetic parameters obtained from the single-crystal studies at liquid-nitrogen temperature are $g_{\parallel} = 2.273 \pm 0.007$, $g_{\perp} = 2.064 \pm 0.008$, $A_{\parallel} = 160 \pm 3 \times 10^{-4} \text{ cm}^{-1}$. At temperatures greater than about 60 °C, the \parallel signal was symmetrical with $g = 2.13 \pm .01$.

The coupling of the unpaired electron with the nitrogen ligands has been measured at liquid-nitrogen temperature. Using this information, we have estimated the ratio of the effective fractional unpaired spin density in a nitrogen p orbital with respect to the s orbital. This ratio was found to be about 2:1. Thus, sp^2 hybridization for the nitrogen ligands seems to be a good approximation.

4.9 Magnetic Properties of Salt Single Crystals at Low Temperatures

B. W. Mangum and R. P. Hudson,

Heat Division

Magnetic susceptibility measurements have been made on a number of rare-earth trichlorides at liquid-helium temperature and below. The results were surprising and substantially different from the known behavior of gadolinium chloride, GdCl_3 , which exhibits a ferromagnetic transition at 2.2 °K.

We have studied cerium chloride, CeCl_3 , praseodymium chloride, PrCl_3 , neodymium chloride NdCl_3 , and samarium chloride, SmCl_3 , all of

which appear to become antiferromagnetic; except for NdCl_3 , however, the evidence is suggestive rather than definitive. In NdCl_3 , the susceptibility between 0.1 °K and 0.9 °K increased with increasing temperature and above 1.8 °K, the reverse was true. Between these regions there are two anomalous, extremely narrow spikes, one at 1.03 °K and the other at 1.75 °K. These spikes are extremely sensitive to an external applied d.c. field; a field of 50 oersteds almost completely eliminates them.

In CeCl_3 we have found a single spike at 0.350 °K below which the susceptibility appears to be constant down to 0.1 °K. Above 0.6 °K a Curie Weiss law is obeyed with a Weiss constant of 0.125 °K.

The susceptibility of PrCl_3 does not even approximate a Curie law in the liquid helium region, the deviation being "antiferromagnetic". A Weiss constant of approximately 1 °K describes the data. Below 1 °K the susceptibility increases slowly with decreasing temperature down to 0.3 °K and displays no spikes.

We have been unable to grow single crystals of SmCl_3 . However, due to the fact that the g-values are almost isotropic, we felt justified in studying a polycrystalline sample. Preliminary data obey the Curie law down to 1.7 °K and show an "antiferromagnetic" departure below this point.

4.10 Spin-Wave Study Using Single Crystals

A. S. Risley and H. E. Bussey,

Radio and Microwave Materials Section

Degenerate spin-wave coupling as a loss mechanism in ferrimagnetic resonance of polycrystalline ferrite has been studied by a new method, that of tilting a spheroid in the magnetic field (Risley and Bussey, 1964). The necessary theory for measuring ferrimagnetic loss by tilting of single-crystal ferrite and garnet spheroids has begun. Also, some experimental work was done on x-ray orientation.

4.11 Reference Data on Single-Crystal Elastic Constants

J. B. Wachtman, Jr., S. Spinner,

and

R. W. Dickson,
Physical Properties Section

Elastic constants of inorganic single crystals are being determined as a basic physical property when suitable single crystals become available. The elastic constants of thorium dioxide, ThO_2 , at 25 °C were determined in collaboration with P. Macedo and W. Capps of the Glass Section (Macedo, Capps, and Wachtman, 1964). The values of four of the elastic constants of TiO_2 have been determined over the range room temperature to 1000 °C (Spinner and Wachtman, 1964).

4.12 Deformation and Fracture of Ionic Crystals

S. Weiderhorn,

Physical Properties Section

The fracture surface energy of soda-lime glass is being studied as a preliminary step to making such measurements on non-cleavable ionic crystals. The double-cantilever cleavage technique as devised by Gilman [J. Appl. Phys., 31, 2208 (1960)] and by Westwood and Hitch [J. Appl. Phys., 34, 3085 (1963)] has been used to obtain fracture energy values of approximately 3370 dynes/cm in liquid nitrogen, 3410 dynes/cm in toluene-solid carbon dioxide, and 2920 dynes/cm in dry nitrogen gas.

Crack motion was observed during the experiment using a 20X microscope. Fracture in all test media occurred in two stages, an initial stage in which the crack velocity remained fairly constant at a value less than 10^{-4} cm/sec and a catastrophic stage in which the crack velocity was greater than 10^{-2} cm/sec and was increasing rapidly. The transition between the two stages occurred rapidly. The initial stage of fracture was greatly dependent on the amount of water vapor present at the crack tip and is believed to be caused by static fatigue in the glass as described by Charles [Prog. in Ceram. Sci., 1, ed. J. E. Burke, Pergamon Press, New York (1961)] and by Charles and Hillig [Symposium on the Mechanical Strength of Glass and Ways of Improving It, Union Scientifique Continentale du Verre (1961)]. In liquid nitrogen, only slight motion occurred before catastrophic failure. In air, 1.5% water vapor, the crack growth preceding catastrophic failure was extensive and was visible to the naked eye. If the initial stage of fracture was in fact due to static fatigue, then it is of interest to note that static fatigue does occur in soda-lime glass at the temperature of liquid nitrogen. The second stage of fracture is believed to be dynamically controlled in the manner described by Berry [J. Mech. Phys. Solids, 8, 194 (1960)].

Further experimentation is planned on glass. It is our intention to extend the measurements to liquid helium temperature and to study the effect of glass composition and surrounding media on the fracture energy of glass.

4.13 Nuclear Magnetic Resonance Studies in Yttrium-Iron Garnets

R. L. Streever,

Magnetic Measurements Section

Using nuclear magnetic resonance techniques, the magnetic characterization of mixed crystals of yttrium iron gallium garnets have been studied as the ferromagnetic iron atoms are replaced by the "non-magnetic" gallium atoms. In addition to measuring the magnetic fields at the nucleus of the ^{57}Fe in these materials, which was the primary objective of the work, we have also been successful in observing the nuclear resonance of ^{69}Ga and ^{71}Ga in these same samples. These latter results are particularly interesting because gallium is a diamagnetic atom and the hyperfine field at the gallium site arises through a transfer of the spin density from the neighboring oxygen

atoms, which are in turn polarized by their neighboring iron atoms. Thus, the hyperfine interaction at the gallium is associated with the superexchange interactions between the gallium and the iron.

A study of the concentration dependence of the hyperfine field has allowed us to separate out the sign and magnitude of the contributions of the hyperfine field from iron in both (a) and (d) lattice sites. Thus, we have been able to obtain an estimate of the relative magnitude of the a-d and the d-d interactions in these materials. The ^{57}Fe studies have also enabled us to estimate the relative number of gallium ions which substitute on to (a) and (d) sites in these materials. This was one of the primary objectives of the work.

From the ^{57}Fe nuclear resonance studied, we have obtained information regarding sublattice magnetizations in these materials as a function of gallium concentration. A paper covering this work (Streever and Urano, 1964) has been published. Another more detailed paper is being prepared and will be submitted for publication in the near future. Future plans involve further studies of these resonances in single crystals of these materials, together with studies of other rare-earth garnets.

4.14 Metal-Oxide Melting Point Standards

S. J. Schneider,

Crystallography Section

Reactions between metal-oxides and suitable container materials such as Ir and W are being investigated to determine possible influence of container materials on the melting behavior of standards (NBS Technical Note 236, Section 4.10).

The Nd_2O_3 -Ir system was the first of a series studied in detail. All experiments were carried out in air inasmuch as Ir has been chosen as the container material for many of the melting point determinations involving an oxidizing environment. The results showed that under equilibrium conditions Ir first oxidizes to IrO_2 and then reacts with Nd_2O_3 to form binary compounds. The Nd_2O_3 - IrO_2 system in air contains two compounds, $3\text{Nd}_2\text{O}_3 \cdot 2\text{IrO}_2$ and $\text{Nd}_2\text{O}_3 \cdot 2\text{IrO}_2$. The former is of unknown symmetry while the latter was identified as a cubic pyrochlore-type compound.

At temperatures above 1300 °C, each of these compounds dissociated to the original mixture of Nd_2O_3 and Ir. Additional heat treatment of the various specimens to 2000 °C indicated that further reactions did not take place in the solid state.

4.15 Soft X-ray Spectroscopy

R. D. Deslattes,

Crystal Chemistry Section

The unavailability of good potassium acid phthalate crystals has continued (NBS Technical Note 236, Section 4.22 and this Note, Section 2.8). This has prevented investigation of the neon K spectrum and

those of sodium and fluorine in NaF (NBS Technical Note 197, Section 3.7). However, the planned automation of the instrument was completed.

Attempts to look with secondary excitation at the valence spectra of III - V compounds and their group IV analogs near 8Å have given very low intensities. It seems that adequate delineation of these profiles requires either a vastly more powerful primary radiation source (possible of the order of 40 kw to generate 1 spectrum per week of continuous operation) or a facility for direct excitation under sanitary conditions. The latter alternative seems more easily realizable and more economical. Preliminary designs are therefore in progress.

Meanwhile, a re-exploration of the krypton L spectrum has begun with special attention to effects of configuration interaction and multiple excitation. These effects naturally occur also in the spectra of crystalline materials where they add to the confusion in sorting out the specifically solid state aspects of these spectra.

4.16 Crystals of Organic Molecules

R. A. Keller and D. E. Breen,

Physical Chemistry Division

Measurements of the extinction coefficient for triplet-triplet transitions in some aromatic hydrocarbons have been completed. The results are given below.

<u>Compound</u>	<u>Wavelength</u>	<u>Extinction Coefficient</u>
naphthalene-h _s	4140 Å	(1.6±0.3) x 10 ⁴ liter/mole cm.
naphthalene-d _s	4140 Å	(1.4±0.3) x 10 ⁴ liter/mole cm.
phenanthrene	4925 Å	(2.7±0.5) x 10 ⁴ liter/mole cm.
triphenylene	4300 Å	(0.7±0.2) x 10 ⁴ liter/mole cm.

These results will be submitted for publication in the near future.

Preliminary measurements have been made on the intramolecular transfer of excitation energy between two isolated chromophors on the same molecule. Work on this project is still in progress.

Some progress has been made on understanding the nature of the interactions involved in intermolecular interactions between two excited triplet molecules. These interactions result in non-radiative deactivation of the triplet state and also give rise to delayed fluorescence.

4.17 Experimental Determination of Atomic Scattering Factors

G. Burley,

Crystallography Section

This is a new project, designed to accurately determine selected atomic scattering factor curves and compare these experimental results with the tabulated theoretical values. The atomic scattering factors for magnesium and oxygen in MgO have now been determined and the results may be summarized as follows:

- 1) Both atoms exist as divalent ions in this structure. The scattering factor curve for the oxygen agrees almost perfectly with that calculated for the O^{-2} anion.
- 2) The scattering factor curve for the magnesium ion deviates considerably from the Hartree-Fock self-consistent field derived value. The experimental values are lower to a $\sin\theta/\lambda$ value of about 0.50\AA^{-1} and then merge with the theoretical result.
- 3) At temperatures above 25°C the difference between the theoretical and experimental results for magnesium gradually decreases, until at about 600°C the two curves become identical. This may indicate a closer approach to spherical symmetry at elevated temperatures.

4.18 Velocity of Sound in Ice Single Crystals*

T. M. Proctor,

Sound Section

The search for a low-temperature vibrational mode in single crystals of ice (NBS Technical Note 197, Section 4.1) is continuing. The determination of the elastic constants from velocity of sound measurements requires that the direction of the acoustic particle motion be known with respect to the crystallographic axes. Ice crystals present a number of environmental problems with regards to the formation and measurement of specific crystallographic orientation. Among these are the facts that ice is not dimensionally stable at normal temperatures, humidities, and pressures and that it cannot be machined at temperatures above -40°C .

Efforts to get around the pressure sensitive freezing point characteristic of ice have led away from the machining operation as a means of sample forming. Instead, crystal samples are grown between two parallel plastic plates. Not only can the shape of the sample be determined this way, but the crystal orientation can be set by the use of a seed crystal. The seed is installed between the plates in such a fashion as to give the desired crystal orientation.

* This work is partially supported by the Office of Naval Research

A special rig is used to position and hold the seed while the growth is carried on. A certain amount of repeat growth is necessary in order to converge on the desired crystal orientation.

With transparent crystals, measurement of crystal orientation is accomplished by standard optical means. This method consists of shining highly convergent polarized light through the crystal. Through the analyzer, a typical interference pattern is seen along the direction of the c-axis for a uniaxial crystal like ice.

For ice, the additional problem of making these orientation measurements under a special environment of very low humidity and of temperature below -10°C exists. An apparatus for this purpose has been constructed and has been used successfully.

An elaborate step-by-step routine is followed in order to keep the dimensions of the sample constant. Several measurements (c-axis orientation, sample thickness, velocity of sound) must be made on one sample. Dimensional changes from condensation, sublimation, and from pressure and temperature melting must be guarded against. The sample's surfaces are kept covered by the plastic plates in which they are grown during the c-axis orientation measurement. The samples thickness must be measured at temperatures of -40°C or lower and in a very dry atmosphere. The whole experiment must be performed quickly so as to minimize the sublimation problem.

4.19 Density Measurements

H. A. Bowman and R. M. Schoonover,

Mass and Volume Section

The Cartesian Diver System is being developed for water-weighing of objects too small for reliable observation on ordinary hydrostatic balances. Such balances of conventional design have uncertainties of 20 micrograms or more; hence, their percentage precision for very small objects is severely limited. Unfortunately, objects of greatest interest in hydrostatic weighing (highly purified substances, single crystals, sensitivity weights, etc.) are not readily available in large sizes. Basically, density determinations are being made by attaching an object to the outside of the Diver and measuring the pressure in the water that will result in zero vertical movement of the Diver. Work to date has consisted of apparatus, and experiments with diver bodies of various hydrodynamic shapes.

At the present state of Diver art, hydrostatic weighings can be made reproducibly to a standard deviation of one or two micrograms. Experiments are conducted on one-gram objects occupying a volume of about $1/20\text{ cm}^3$. This precision is comparable to that obtained in a high quality air weighing. Efforts at present are being devoted to obtaining volumetrically stable objects which can be used as comparison standards in Diver weighings. Experiments are being conducted on nichrome and gold, with platinum, fluxed quartz and pyrex to follow shortly. As soon as stable standards are developed and calibrated against mercury, they will be compared hydrostatically with various single crystals, probably beginning with rutile.

The density of near perfect single crystals is an important parameter in the crystal characterization program, because, in some cases, lattice defects and impurities are most easily detectably by density differences.

4.20 Superconductivity in Niobium

V. D. Arp,

Cryogenic Properties of Solids Section

Fermi-surface properties of niobium are responsible for ideal class II super-conducting properties of the highly purified metal. Measurements of the anomalous skin effect and magnetoresistance are under way to provide more detailed information on certain of these relations.

In the process, we have annealed commercially available niobium to achieve a resistance ratio ($R_{300\text{ }^\circ\text{K}}/R_{4\text{ }^\circ\text{K}}$) of 300 in a polycrystalline sample. Results of measurements are expected later this year.

4.21 Research on Superconducting Semiconductors

J. Schooley and E. Ambler
Cryogenic Physics Section

and

W. R. Hosler and J. H. Becker
Solid State Physics Section

The discovery of superconductivity in the semiconductor strontium titanate, SrTiO_3 , by measurements below 1 °K of electrical resistivity and magnetic susceptibility (Schooley, Hosler, and Cohen, 1964) has taken place through the cooperative efforts of the Cryogenic Physics and Solid State Physics Sections. This resulted from the unique low-temperature facilities and techniques, and extensive energy-band studies on SrTiO_3 , (see Technical Note 236; Frederikse, Thurber, and Hosler, 1964); (Kahn and Leyendecker, 1964 and Kahn, Frederikse, and Becker, 1963) coupled with recent applications of the BCS theory [Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957)] of superconductivity to multivalently semiconductors (Cohen, Phys. Rev. 134, A511, 1964). The importance of this subject lies in the ease of testing theories of superconductivity, and possible technological applications which may result from the extended knowledge.

Studies on SrTiO_3 are continuing. Preliminary data of four-terminal resistance indicate that the superconducting transition temperature T_c (defines here as the temperature for which $R/R_{\text{normal}} = 0.5$) depends on electron concentration n approximately as:

$$T_c (\text{H}_2\text{O}) \text{ }^\circ\text{K} = 0.7 \exp(-3.07 \times 10^6 n^{-1/3})$$

for $n \sim 10^{18}$ to $3 \times 10^{19}/\text{cc}$ with a maximum in T_c of ~ 0.3 °K occurring for n between 5×10^{19} and $10^{20}/\text{cc}$.

A wide variety of other materials is also being studied. The select-

ion of these is based on theoretical principles and limited information of physical properties available in the literature.

4.22 Optical Properties of Cadmium Sulfide and Telluride*

L. H. Grabner and R. C. Keezer,
Solid State Physics Section

Investigation of the quenching of photoconductivity of CdS near the absorption edge is nearing completion. In addition to the experimental facts summarized in Technical Note 236, Section 3.18, photoconductivity peaks have been identified as due to excitation of free excitons from the three valence bands of CdS. These are observed at temperatures as high as room temperature and permit a determination of the bandgap as a function of temperature to three significant figures. The mechanism of quenching previously thought to be due to the shortening of the lifetime of a bound exciton by induced emission may have to be modified by our inability thus far to detect the quenching at temperatures of 10 °K. Acceptor levels close to the conduction band may be responsible. A defect of this kind has been observed by M. R. Lorenz and H. H. Woodbury [Phys. Rev. Letters, 10, 215 (1963)] in CdS and CdTe by transport measurements.

4.23 Soft X-ray Spectroscopy of Metals and Alloys

J. R. Cuthill and M. L. Williams
Alloy Physics Section

A 2-meter, grazing incidence, soft X-ray spectrometer employing a 30,000 lines/inch grating and a Bendix strip multiplier detector has been built. The instrument covers the spectral region of 25 to 800Å and will be employed to observe the characteristic X-ray spectra corresponding to transitions from the valence band to the outermost normally filled level. The distribution of occupied states in the valence band is related to this spectra through the transition probability coefficients involved. Of particular interest in the NBS program is the study of change in the density-of-state distribution upon the formation of congruent melting, intermetallic compounds. Single crystal specimens will be included and the effect of cold working will be studied.

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

5. CRYSTAL CHEMISTRY

This chapter is concerned with studies of **crystal** structure, phase relations, and other chemical properties not sensitive to crystal perfection.

5.1 Standard X-ray Diffraction Powder Patterns*

H. E. Swanson,

Crystallography Section

Diffraction patterns are produced in a continuing program for the Powder Data File, a reference compilation for identification of crystalline materials. The NBS patterns have been published in thirteen volumes as Circular 539 and Monograph 25. The latest issue (Swanson, Morris, Evans, and Ulmer, 1964) includes primarily, inorganic compounds. For materials with simple structure and which are difficult to obtain, calculated patterns are now being prepared.

Improved reliability in cell dimension is now being sought for internal standards of silver, tungsten, and cadmium oxide through carefully controlled measurements of several samples.

5.2 Apparatus for High-Temperature Preparation of Pure Crystalline Polymorphs

A. R. Glasgow, Jr.,

Analysis and Purification Section

A special cell was designed for use to 1000 °C in phase purifications and thermal analysis for the purification of 20-40g amounts of pure polymorphic crystalline forms of BeF_2 .

Three metals are used in the fabrication; inconel to withstand oxidation at high temperatures, nickel to withstand fluorides at high temperatures, and monel to resist attack by both oxygen and fluorides at lower temperatures. Access to the cell is through a high-vacuum coupling of monel at the top, which contains an opening for evacuation and pressure control. One part of the coupling is welded to the double walls of inconel and nickel comprising the shell and the other to the double walls comprising a re-entrant coolant well. Thus, the inner system is all nickel and the outer - all inconel in the portions subjected to high temperatures. The cell is provided with removable nickel vessels at the bottom, lower-center, and top, in which the products as solids can be removed after phase separations involving distillation, preferential decompositions, sublimation, and crystallization.

* This work is partially supported by the Joint Committee on Chemical Analysis by X-Ray Diffraction under the auspices of the American Society for Testing and Materials, The American Crystallographic Association, The British Institute of Physics, and the National Association of Corrosion Engineers.

The operations are performed with the cell placed in a vertical position in a three-zone control furnace. For thermal analysis, two thermocouples are located in the well and two at the bottom of the cell.

Careful attention was given in the design of the cell to details of simplicity, chemical inertness, thermal expansion, mechanical strength, measurement, and control of temperature and temperature gradients, and flexibility in operation. As a result, with the new equipment, much higher temperatures (up to 1000 °C) and much more favorable conditions for thermal analysis for the detection of polymorph formation should be available. This cell was completed by our shops on July 7, 1964, and is now being put into service.

5.3 Fermi Resonance in Solids

S. Abramowitz and J. J. Comeford,

Heat Division

The infrared absorption spectra of CF_4 and CCl_4 have been observed in both pure form and in rare gas matrices at low temperatures. The region studied corresponded to the ν_3 , $2\nu_4$, and ν_3 , $\nu_1 + \nu_4$ Fermi doublets of CF_4 and CCl_4 , respectively. The interactions of the vibrations involved in the resonance in these molecules changes considerably from that found in the gas phase. The results are consistent with recent theories.

5.4 Crystal Structure Analysis

S. Block, H. M. Ondik, A. Perloff,

and

L. H. Hall,
Crystallography Section

The structure of SrB_4O_7 , which was recently completed has revealed an unusual borate network. All the boron atoms are tetrahedrally coordinated. Furthermore, one oxygen atom is coordinated to 3 boron atoms. The projection of the structure on the ab plane is shown in Figure 23. The numbers indicate fractional z coordinates. The unique oxygen is at $z = .22$. This structure, when compared with that of BaB_4O_7 , shown in Figure 24, indicates that the coordination of boron cannot be simply correlated with composition. Although BaB_4O_7 has the same boron-oxygen content as the strontium compound, half of the boron is triangularly coordinated by oxygen, while the other half is tetrahedrally coordinated.

Other work includes the first complete structure determination of a halogenated boron hydride (iodopentaborane). The investigation was carried out at -25 °C and showed, in agreement with NMR spectra, that the iodine is bonded to the apical boron.

Complete 3 dimensional data for bis-carborane has been collected with a counter diffractometer and CuK_α radiation. It is hoped that a new method will be useful for computing the structure.

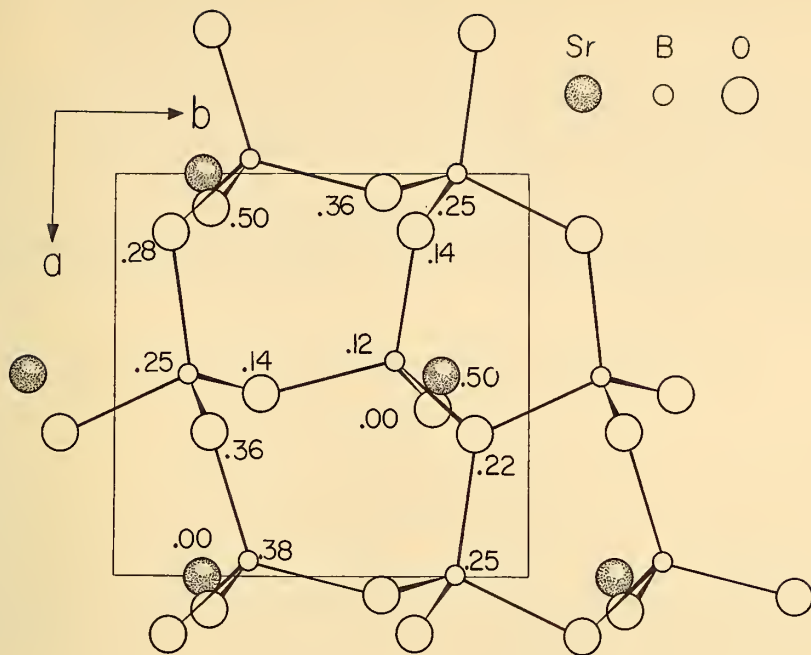


Fig. 23. Projection of structure of SrB_4O_7 on the ab plane.

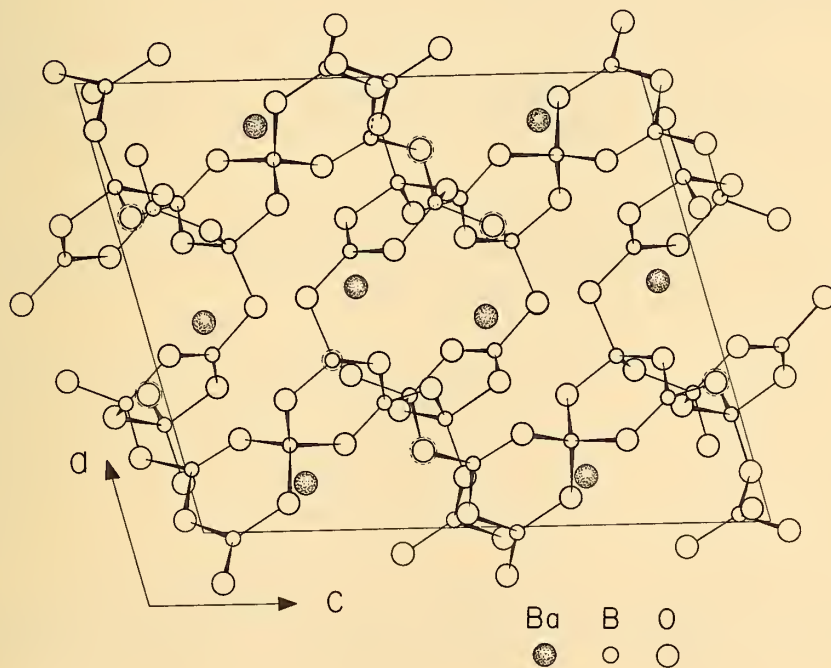


Fig. 24. Projection of structure of BaB_4O_7 on the ac plane.

Single crystals of the low temperature form of Li_3PO_4 have been grown and the structural relationship of the high and low temperature forms is being investigated by single crystal techniques.

The determination of the structure of the triclinic form of sodium tetrametaphosphate tetrahydrate (Ondik, 1964a) showed that its relationship with the monoclinic form was that of packing. Both forms have similar phosphate rings.

The structures of the pair, $\text{Na}_3\text{P}_3\text{O}_9$ and $\text{Na}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$, were determined and revealed the interesting phenomena of a hole occurring in the anhydrous form. This hole is filled by the water molecule in the hydrate (Ondik, 1964b).

5.5 Crystal Chemistry of Mineralized Tissue

W. E. Brown and E. C. Moreno,

Dental Research Section

It is well accepted that the principal inorganic constituent in tooth and bone is hydroxyapatite. Its unique structural relationship to hydroxyapatite has introduced the possibility that octacalcium phosphate is of great significance in physiological systems. We have proposed that its role is largely a transitory one, but by participating in the formation of the crystallites of tooth and bone it contributes materially to their chemical and physical properties. Octacalcium phosphate appears to participate in the growth processes in at least two important ways.

1. It provides the seed or nucleus on which the hydroxyapatite is later deposited. In enamel, this seed is a ribbon, possibly of unit-cell thickness, of octacalcium phosphate. In bone and other precipitates, it is thought that the same nuclei are present but in much less elongated form.

2. Subsequent growth of apatitic crystals may take place through a two-step mechanism requiring alternately the laying down of a unit-cell thickness of octacalcium phosphate followed by its hydrolysis to a two unit-cell thickness of hydroxyapatite.

5.6 Phase Equilibria

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

Crystallography Section

In a continuation of studies on the polymorphism of Bi_2O_3 (Levin and Roth, 1964), the heats of transformation of Bi_2O_3 were determined by differential thermal analysis. The values obtained were: Bi_2O_3 transition (monoclinic $\xrightarrow{730^\circ\text{C}}$ cubic) - 9.9 kcal/mol and Bi_2O_3 fusion (cubic $\xrightarrow{825^\circ\text{C}}$ liquid) - 3.95 kcal/mol. A value of 2.05 kcal/mol for the heat of fusion was obtained earlier [E. M. Levin and C. L. McDaniel, J. Am. Ceram. Soc., 45, 355 (1962)] from the slope of the liquidus curve in the Bi_2O_3 - B_2O_3 diagram.

Solid state studies in the system $\text{Nb}_2\text{O}_5\text{-TiO}_2$ (Waring and Roth, 1964) have lead to the discovery of a series of tetragonal phases of the general type $10\text{M}_3\text{O}_5 \cdot 90\text{M}'_2\text{O}_5$ where M is P, As, Ge, or V and M' is Nb or Ta. These phases are apparently isostructural with $\text{Ta}_2\text{O}_5 \cdot 2\text{Nb}_2\text{O}_5$.

The compound FeNbO_4 has been found to be trimorphic (Roth and Waring, 1964). The low temperature (monoclinic) form transforms at about 1085°C to an orthorhombic ixiolite type which, in turn, transforms to a third form at 1475°C which is isostructural with rutile.

5.7 Radial Distribution Studies of Glasses

S. Block, A. Hyman, and G. Piermarini,

Crystallography Section

Radial distribution studies on vitreous and crystalline borates (NBS Technical Note 236, Section 5.11) have been continued. An analysis of radial distribution curves obtained earlier (Piermarini and Block, 1963) [Block, Molin, and Piermarini, J. Am. Ceram. Soc., 46, 557 (1963)] shows that a model based on random packing of hard spheres cannot adequately account for the shape of these curves. The modifier-oxide cations must be assumed to occupy positions which show some degree of order. An electron-pair distribution function has been derived. The function was used to obtain a distribution curve for crystalline $\text{BaO} \cdot 2\text{B}_2\text{O}_3$. The similarity of this curve and the curve for vitreous barium borate (1:1.7) indicates similar short-range order in the crystal and the glass. A paper concerning the distributions of alkaline-earth cations in vitreous borates (Block and Piermarini, 1964a) presents a detailed discussion of these results.

5.8 Allotropy in the Rare Earth Metals

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

Crystallography Section

The survey of effects of pressure on the structures of the rare earth metals (NBS Technical Note 236, Section 5.6) is being continued. A paper on the allotropic modifications in lanthanum, cerium, praseodymium, and neodymium has been published (Piermarini and Weir, 1964) and work on the structures of the metals samarium, gadolinium, and terbium up to pressures of 35 - 40 kb has been completed using the high-pressure x-ray powder diffraction camera described earlier [Piermarini and Weir, J. Research NBS 66A, 325 (1962)]. These studies revealed no new allotropic forms in this pressure range. Cerium metal was studied at pressures up to about 120 kb. The electronic transition (fcc to "collapsed" fcc) occurring at about 7.5 kb was corroborated, and, in addition, evidence for a second allotropic form which has been reported was found at pressures of 110 - 120 kb. Further investigation of this new form is planned.

The high pressure x-ray camera has been substantially redesigned to provide a greater angular range. This camera will be used in subsequent studies on the rare-earths.

5.9 Infrared Studies of Inorganic Materials

C. Weir and R. A. Schroeder,

Crystallography Section

Infrared studies of B^{10} and B^{11} substituted anhydrous borates were carried out in the 2000 cm^{-1} - 300 cm^{-1} range. Spectral bands for all ortho-, pyro-, and some meta-borates could be assigned satisfactorily. From correlations between spectra and structure, it appears that boron in 3 fold or in 4 fold coordination can be identified on the basis of the infrared spectrum alone. Triangularly coordinated boron is characterized by the presence of strong, broad absorption in the 1100 cm^{-1} - 1300 cm^{-1} region. In addition, there is absorption in the 700 cm^{-1} region. Both of these characteristic bands are strongly dependent on isotope mass and thus isotopic substitution can be used to differentiate these bands from others occurring in these regions.

The most characteristic feature of tetrahedrally coordinated boron is the presence of strong, broad absorption in the 800 cm^{-1} - 1100 cm^{-1} region. Also, absorption bands which are not sensitive to isotope mass and therefore can be distinguished from triangular boron, occur in the 700 - 800 cm^{-1} region (Weir and Schroeder, 1964). These studies were used to predict that tetrahedral coordination of boron occurs in SrB_4O_7 . This was confirmed by single crystal studies.

5.10 Structure Models for Amorphous and Crystalline Phases of Simple Substances

Fred Ordway,

Inorganic Materials Division

Computer routines have been completed for processing measurements on the random tetrahedral network of 300 units. Computations include: coordinates from angle measurements; generations of remaining points of a unit when only three are known; generation and deletion of coordinate listings implied by topological data; checking dimensions of units; reconciling multiple sets of coordinates for the same point; checking sets for completeness; tabulating distributions of distances and angle, listing those beyond tolerance limits; and adjusting positions for best agreement with ideal distances. Coordinate data for the model have been completed and adjusted, and some of the distributions calculated. Aspects of the work were described in lectures at Corning Research Laboratories, Alfred University, and Harvard University, and in a publication (Ordway 1964).

5.11 Crystal Chemistry of Silver Iodide*

G. Burley,

Crystallography Section

Previous work in this area was discussed in NBS Technical Note 236. Studies of the kinetics and mechanism of the low-cubic to hexagonal phase transformation (Burley, 1964a) and of an x-ray determination of the Debye temperature of silver iodide (Burley, 1964b) have been published. A paper discussing an x-ray investigation of strain in silver iodide as well as another treating the ice nucleation by photolyzed silver iodide particles have been accepted for publication. An analysis of the radial distribution data of powder x-ray diffraction data from both the low-cubic and hexagonal phases just above the transition temperature of both to the high-cubic structure at 147°C is continuing.

5.12 A New High-Resolution Small-Angle X-Ray Camera

H. Brumberger** and R. Deslattes

Crystal Chemistry Section

This instrument was described in NBS Technical Note 236, Section 5.12. The following is the abstract of a paper (Brumberger and Deslattes, 1964):

"A novel small-angle x-ray camera, utilizing the Borrmann effect in the 220 Laue reflection from germanium to form the incident beam, has been designed and tested. A test pattern of amorphous carbon showed angular resolution to nearly 2000 Å. In principle, an improvement of resolution by an order of magnitude is possible."

5.13 Spectroscopy of Diatomic Impurities in Rare-Gas Crystalline Matrices

L. Pollack,

Crystal Chemistry Section

The abstract of a paper published during the reporting period follows (Pollack and Pollack, 1964):

"Examination of absorption spectra of molecules in liquid and crystalline matrices gives

*Research supported by the Atmospheric Sciences Program, National Science Foundation, NSF Grant G 19648

**On research leave of absence from Dept. of Chemistry, Syracuse University, Syracuse 10, N. Y.

information on two fundamental kinds of problems: perturbations of molecules by surrounding fields, and effects of impurities on crystals and crystal growth. Rare-gas solid and liquid matrices are ideally suited to such problems since the forces between rare-gas atoms are especially weak, symmetric, short-range, and well known. Experimental studies of growth and observation of pure rare-gas crystals, transparent in a broad range from the infrared to the vacuum ultra-violet, and of low concentrations of diatomic molecules in solid solution with rare gases are described. As an example, the system NO in liquid and crystalline Kr was studied in the range from 2000-5000 Å. Even at the smallest concentrations of NO no trace of discrete spectra of the NO γ system was found. However, a cutoff at short wavelength was observed in the liquid, increasing with NO concentration. This absorption cutoff may be due to the transition from the ground state X² π to the theoretically predicted ⁴ π state. Both spectroscopic and solid state conclusions are drawn from these experiments and experiments on other systems of the same kind."

5.14 Crystal - Field Studies by Matrix Spectroscopy

D. E. Mann,

Molecular Spectroscopy Section

The extensive investigation by infrared spectra of HCl and DC1 in solid argon and krypton has been completed. In addition to demonstrating the existence of molecular rotation the results provided new evidence of the influence of impurities on the spectra and motions of the diatomic species and showed the theoretical analysis formulated by Flygare to be incorrect. The study of other diatomic molecules, including HBr and CO, in rare-gas matrices is being continued along the lines already developed for HCl with promising results.

5.15 Phase Equilibria Determination with the Aid of Crystal Structure Analysis

R. S. Roth*,
Crystallography Section

and

A. D. Wadsley**

The crystal structures of the compounds $P_2Nb_{18}O_{50}$ and $TiNb_{24}O_{62}$ were determined by x-ray methods. Knowledge of the structure of these compounds of Nb_2O_5 , and of other titano-niobates was used to predict phases that might be expected to occur in other chemical systems involving Nb_2O_5 .

In the system $Nb_2O_5-WO_3$, five new compounds, three monoclinic and two tetragonal, were found in the composition range 0 - 51% WO_3 which had previously been described as a solid solution range. The crystal structures of four of these compounds were determined and some general rules for the occurrence of various phases in niobate systems were formulated. The phase equilibrium diagram for the entire system $Nb_2O_5-WO_3$ is now being determined, and the crystal structure of other compounds in the system is under investigation.

A paper on composition of the phases in the systems $NbO_2-Nb_2O_5$ and $TiO_2-Nb_2O_5$ (Roth, Wadsley, and Gatehouse, 1964) has been published. A second on mixed oxides of titanium and niobium and the crystal structure of $TiO_2 \cdot 12Nb_2O_5$ (Roth and Wadsley, 1964) has been accepted, and a third on the crystal structure of $P_2O_5 \cdot 9Nb_2O_5$ is in preparation.

5.16 Ultrasonic Measurements at Pressure-Induced Polymorphic Phase Changes

P. Heydemann,

Pressure Measurements Section

An attempt will be made to measure the change of the elastic constants and of the internal friction of crystals at ultrasonic frequencies during pressure-induced changes of their crystal structure. These measurements will be combined with electrical and PVT-measurements. Among the materials to be studied are potassium chloride and bismuth. Both single and polycrystalline samples will be used. An apparatus is being developed which will allow the determination of the transition pressures with great precision.

* This work was completed at CSIRO, Melbourne, Australia while Dr. Roth was on Educational Leave. He has since returned to NBS.

** Dr. A. D. Wadsley, Mineral Chemistry Division, CSIRO, Melbourne, Australia.

5.17 Microcomposition and Structure Characterization
by Electronprobe Methods

H. Yakowitz and D. Vieth

Lattice Defects and Microstructures Section

and

J. R. Cuthill

Alloy Physics Section

An electronprobe microanalyzer was built at NBS before commercial instruments became available. Chemical analyses of regions of the order of one micron in diameter can be made in situ by excitation of such a region with a focused beam of electrons and analysis of the characteristic x-ray emission produced. One of the studies made with this instrument was a study of the uniformity of chemical composition of the NBS 461 standard steel sample (Michaelis, Yakowitz, and Moore, 1964). This standard sample material was found to be chemically uniform at the two to four micron level of spatial resolution.

This original NBS electronprobe has been rebuilt with a higher take-off angle to permit analysis of the light elements, and with provision for obtaining Kossel patterns. The Kossel pattern technique is the most sensitive and accurate method for obtaining local changes in lattice spacings, as might be introduced by local strains, and the electronprobe is ideally suited to this technique. The first-named of the above investigators has just returned after a year of study at MIT under Prof. Ogilvie, acquiring experience in applying the Kossel technique with the electronprobe.

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:

Abramowitz, Stanley: Ph.D. Polytechnic Inst. of Brooklyn, 1963; infrared molecular spectra; Heat Division Author: 5.3
Allen, Harry C., Jr.: Ph.D. University of Washington 1951; electron-spin-resonance studies; Chief, Inorganic Materials Division Author: 4.8
Ambler, Ernest: Ph.D. Oxford University, 1953; nuclear reactions, low-temperature magnetism; Chief, Cryogenic Physics Section, Heat Division Author: 4.21
Barber, David J.: Ph.D. University of Bristol, 1959; growth perfection of crystals; Physical Properties Section, Inorganic Materials Division Author: 3.11
Bass, Arnold M.: Ph.D. Duke University 1949; molecular spectroscopy; Heat Division

Becker, James H.: Ph.D. Cornell University, 1957; optical and transport properties of semiconductors; Solid State Physics Section, Atomic Physics Division Author: 4.21, 4.4

Bennett, Laurence H.: Ph.D. Rutgers University, 1958; nuclear resonance studies; Chief, Alloy Physics Section, Metallurgy Division Author: 3.8

Block, Stanley: Ph.D. Johns Hopkins University, 1955; x-ray crystallography; Crystallography Section, Inorganic Materials Division Author: 5.4, 5.7

Blunt, Robert F.: Ph.D. Rice University, 1949; optical properties of solids; Solid State Physics Section, Atomic Physics Division Author: 3.1

Bolz, Leonard H.: Crystal perfection by electron microscopy; Physical Properties Section, Inorganic Materials Division

Bowman, Horace A.: Cartesian diver; Mass and Volume Section, Metrology Division Author: 4.19

Breen, David E.: Inter- and intramolecular properties of organic molecules, crystals, and rigid glasses; Physical Chemistry Division Author: 4.16

Brower, William S.: Crystal growth by Verneuil process and floating-zone technique; Crystal Chemistry Section, Inorganic Materials Division Author: 2.6

Brown, Walter E.: Ph.D. Harvard University, 1949; solubility and crystallography of calcium phosphate; Dental Research Section, Polymers Division Author: 5.5

Burley, Gordon: Ph.D. Georgetown University, 1962; crystallography of silver iodide; Crystallography Section; Inorganic Materials Division Author: 4.17, 5.11

Calvert, Joan P.: Growth of oxide films; Corrosion Section, Metallurgy Division

Capps, Webster: Physics and chemistry of glass; Glass Section, Inorganic Materials Division

Cataland, George: Low-temperature thermometry; Cryogenic Physics Section, Heat Division

Chang, Te-Tse: Ph.D. Univ. of Colorado, 1962; magnetic resonance; Solid State Physics Section, Atomic Physics Division Author: 3.15

Cohen, Martin L.: X-ray diffraction studies of crystals grown at high temperatures; Solid State Physics Section, Atomic Physics Division Author: 3.2

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

Comeford, J.J.: Molecular spectroscopy; Molecular Spectroscopy Section, Physical Chemistry Division Author: 5.3

Cooter, Irvin L.: Nuclear magnetic resonance in garnets; Chief, Magnetic Measurements Section, Electricity Division

Coriell, Sam R.: Ph.D. Ohio State University, 1961; mathematical physics; Crystallization of Metals Section, Metallurgy Division Author: 2.3

Cuthill, J.R.: Ph.D. Purdue University, 1952; soft x-ray spectroscopy, electroprobe electron analysis; Alloy Physics Section, Metallurgy Division Author: 5.17

deKoranyi, Alexandra: Crystal growth by electrodeposition; Electrolysis and Metal Deposition Section, Metallurgy Division Author: 3.6

Deslattes, Richard D.: Ph.D. Johns Hopkins University, 1959; x-ray spectroscopy; Crystal Chemistry Section, Inorganic Materials Division Author: 3.14, 4.5, 4.15, 5.12

deWit, Roland: Ph.D. University of Illinois, 1959; dislocation theory; Lattice Defects and Microstructures Section, Metallurgy Division Author: 3.5

Dickson, Robert W.: Homogeneous stress on oxide structures, dislocation studies by x-ray methods; Physical Properties Section, Inorganic Materials Division Author: 2.1

Dove, Robert B.: Nuclear magnetism; Cryogenic Physics Section, Heat Division

Dueker, Heyman C.: Ph.D. University of Maryland, 1964; physical chemistry of glasses; Glass Section, Inorganic Materials Division
Early, James G.: Ph.D. Rennsalaer Polytechnic Inst., 1963; kinetics of crystallization; Crystallization of Metals Section, Metallurgy Division Author: 2.2
Eby, Ronald K.: Ph.D. Brown University, 1958; acoustics, polymer physics; Polymer Physics Section, Polymers Division Author: 2.19
Edlow, Martin E.: Low-temperature thermometry; Cryogenic Physics Section, Heat Division
Eisenstein, Julian C.: Ph.D. Harvard University, 1948; low temperature magnetism; Cryogenic Physics Section, Heat Division
Escalante, Edward: Field emission; Corrosion Section, Metallurgy Division
Evans, Eloise H.: Physical chemistry, x-ray diffraction; Crystallography Section, Inorganic Materials Division, A.S.T.M. Fellowship supported
Farabaugh, Edward N.: Etch-pits crystal orientation; Crystal Chemistry Section, Inorganic Materials Division Author: 4.1
Foley, Carol L.: Growth of oxide films; Corrosion Section, Metallurgy Division Author: 3.7
Forman, Richard A.: Nuclear and quadrupole resonances; Solid State Physics Section, Atomic Physics Division Author: 3.15
Franklin, Alan D.: Ph.D. Princeton University, 1949; properties of point defects in crystals; Inorganic Materials Division
Frederickse, Hans P. R.: Ph.D. Leiden University, 1950; semiconductors at low temperatures; Chief, Solid State Physics Section, Atomic Physics Division Author: 4.4
French, Judson C.: Solid state devices and materials; Electron Devices Section, Instrumentation Division Author: 3.10
Frolen, Lois J.: Ph.D. Pennsylvania State University, 1963; spectroscopy, crystallography, microscopy; Polymers Division Author: 2.14, 2.15
Glasgow, Augustus R.: D.Sc. University of Brussels, 1957; preparation and purification of polymeric forms, phase equilibria, purity determinations at high pressures; Analytical and Purification Section, Analytical Chemistry Division Author: 2.8, 5.2
Gornick, Fred: Ph.D. University of Pennsylvania, 1959; physical chemistry of high polymers; Polymers Division Author: 2.15
Grabner, Ludwig H.: Ph.D. Columbia University, 1950; semiconductors, photoconductivity; Solid State Physics Section, Atomic Physics Division Author: 4.22
Hall, L. H.: Ph.D. Johns Hopkins University, 1963; crystal structures; Crystallography Section, Inorganic Materials Division Author: 5.4
Haller, Wolfgang K.: Ph.D. University of Vienna, 1950; physical chemistry of glasses; Glass Section, Inorganic Materials Division
Hardy, Stephen C.: Vapor growth of metal crystals; Crystallization of Metals Section, Metallurgy Division Author: 2.4
Harman, George G.: Solid state physics, surface phenomena and electroluminescence; Electron Devices Section, Instrumentation Division Author: 3.10
Heydemann, Peter: Ph.D. University of Göttingen, 1958; physical acoustics, mechanical and electrical properties of polymers; Pressure Measurement Section Author: 5.16
Hoffman, John D.: Ph.D. Princeton University, 1949; dielectrics, nucleation rate of polymer crystals; Chief, Polymers Division
Holly, Sylvanus: Crystal growth; Crystal Chemistry Section, Inorganic Materials Division
Horton, Avery T.: Crystal growth, impurity retention; Crystal Chemistry Section, Inorganic Materials Division Author: 2.7
Hosler, William R.: Electronic transport phenomena; Solid State Physics Section Author: 4.4, 4.21
Howard, Robert E.: Ph.D. Oxford University, 1957; theoretical physics; Chief, Metal Physics Section, Metallurgy Division Author: 2.20, 3.5

Hudson, Ralph P.: Ph.D. Oxford University, 1949; low-temperature magnetism; Chief, Heat Division Author: 4.9

Hyman, A.: Ph.D. Rutgers, 1964; physical chemistry; Crystallography Section, Inorganic Materials Division Author: 5.7

Ives, Lewis K.: Electron microscopy; Lattice Defects and Microstructures Section, Metallurgy Division Author: 3.3

Jackson, Ronald W.: Ph.D. University of Bristol, 1950; thermodynamics of sucrose solutions, kinetics of growth of sucrose crystals; Crystal Chemistry Section, Inorganic Materials Division Author: 2.12

Kaesler, Robert S.: Low-temperature magnetism, cryogenics; Cryogenic Physics Section, Heat Division

Kahn, Arnold H.: Ph.D. University of California, 1955; electronic energy levels of solids; Solid State Physics Section, Atomic Physics Division Author: 4.3

Keezer, Richard C.: Optical properties and physical chemistry of semiconductors; Solid State Physics Section, Atomic Physics Division Author: 4.4, 4.22

Keller, Richard A.: Ph.D. University of California, 1961; inter- and intramolecular properties of organic molecules, crystals, and rigid glasses; Physical Chemistry Division Author: 4.16

Khoury, Fred: Ph.D. Leeds University, 1956; morphology and crystallization of polymers; Polymer Physics Section, Polymers Division Author: 2.17

Klein, Ralph: Ph.D. University of Pittsburgh, 1950; field-emission and low-temperature chemistry; Chief, Surface Chemistry Section, Physical Chemistry Division

Kokoszka, Gerald F.: Electron-spin-resonance studies; Inorganic Materials Division Author: 4.8

Kruger, Jerome: Ph.D. University of Virginia, 1953; corrosion reactions at metal surfaces; Corrosion Section, Metallurgy Division Author: 3.7

LaVilla, Robert E.: Ph.D. Cornell University, 1960; diffraction techniques; Crystal Chemistry Section, Inorganic Materials Division Author: 4.5

Levin, Ernest M.: Phase equilibria of oxide systems; Crystallography Section, Inorganic Materials Division Author: 5.6

Lippincott, Ellis R.: Ph.D. Johns Hopkins University, 1947; infrared spectroscopy; Crystallography Section, Inorganic Materials Division

Macedo, P. B.: Ph.D. Catholic University, 1963; viscoelastic properties; Glass Section, Inorganic Materials Division

Mangum, Billy W.: Ph.D. University of Chicago, 1961; low-temperature magnetism; Cryogenic Physics Section, Heat Division. Author: 4.9

Mann, David E.: Ph.D. University of Chicago, 1948; spectroscopy; Chief, Molecular Spectroscopy Section, Physical Chemistry Author: 5.14

Mante, Alexander J. H.: NATO Fellow (1963-1964); theomoelectricity; Solid State Physics Section, Atomic Physics Division. Author: 4.4

Margoshes, Marvin: Ph.D. Iowa State University, 1953; spectrographic analysis; Spectrochemical Analysis Section, Analytical Chemistry Division Author: 3.9

Marshak, Harvey: Ph.D. Duke University, 1955; nuclear reactions, cryogenics; Cryogenic Physics Section, Heat Division

Martin, G.M.: Polymer physics; Polymer Physics Section, Polymers Division Author: 2.18

Marvin, Robert S.: Ph.D. University of Wisconsin, 1949; rheology and polymer physics; Chief, Rheology Section, Mechanics Division

Marzullo, Sam: Dielectric properties; Physical Properties Section, Inorganic Materials Division

Mauer, Floyd A.: Instrumentation for crystallography; Crystallography Section, Inorganic Materials Division Author: 3.16

McMurdie, Howard F.: Crystallography and chemical phase studies; Chief, Crystallography Section, Inorganic Materials Division

McNish, Alvin G.: Precise density determinations for solid materials; Chief, Metrology Division
Mebs, Russell W.: Ph.D. Ohio State University, 1940; nuclear acoustic resonance; Alloy Physics Section, Metallurgy Division
Melmed, Allen J.: Ph.D. Pennsylvania State University, 1958; surface studies by field emission; Corrosion Section, Metallurgy Division
 Author: 2.5
Miller, Paul R.: High-temperature crystal growth, crystal orientation; Crystal Chemistry Section, Inorganic Materials Division. Author: 4.1
Milligan, Dolphus E.: Ph.D. University of California, 1958; molecular spectroscopy; Molecular Spectroscopy Section, Physical Chemistry Division
Moreno, E. D.: Ph.D. University of California, 1957; physical chemistry of calcium phosphates; Dental Research Section, Polymers Division
 Author: 5.5
Morris, Marlene C.: Physical Chemistry, x-ray diffraction; Crystallography Section, Inorganic Materials Division; A.S.T.M. Fellowship supported
Newton, Clarence J.: Ph.D. University of Texas, 1952; x-ray crystallography of metals; Lattice Defects and Microstructures Section, Metallurgy Division
 Author: 3.4
Ogburn, Fielding: Electrochemistry, electrodeposition; Electrolysis and Metal Deposition Section, Metallurgy Division
 Author: 2.10, 3.6
Ondik, Helen M.: Ph.D. Johns Hopkins University, 1957; crystallography, inorganic chemistry; Crystallography Section, Inorganic Materials Division
 Author: 5.4
Ordway, Fred: Ph.D. California Institute of Technology, 1949; x-ray crystallography; Inorganic Materials Division
 Author: 5.10
Orem, Theodore H.: Mechanisms of corrosion processes; Crystallization of Metals Section, Metallurgy Division
 Author: 2.1
Oser, Hans J.: Ph.D. University of Freiburg, 1957; boundary value problems; Applied Mathematics Division
 Author: 2.20
Paretzkin, Boris: Study of perfection of single crystals by x-ray diffraction; Crystal Chemistry Section, Inorganic Materials Division
 Author: 2.11, 3.15
Parker, Harry S.: Ceramic engineering; Crystal Chemistry Section, Inorganic Materials Division
 Author: 2.12
Parker, Robert L.: Ph.D. University of Maryland, 1960; growth of crystals; Chief, Crystallization of Metals Section, Metallurgy Division
 Author: 2.1, 2.2, 2.3, 2.4, 2.20
Passaglia, Elio: Ph.D. University of Pennsylvania, 1955; mechanical relaxation processes in polymers; Polymer Physics Section, Polymers Division
 Author: 2.18
Payne, Richard E.: Nuclear resonance; Solid State Physics Section; Atomic Physics Division
Peiser, H. Steffen: Crystallography and crystal chemistry; Chief, Crystal Chemistry Section, Inorganic Materials Division.
 Author: 2.10, 4.2
Perloff, Alvin: Structure analysis; Crystallography Section, Inorganic Materials Division
 Author: 5.4
Pfeiffer, Earl R.: Crystal growth from solution; Cryogenic Physics Section, Heat Division
Piermarini, Gaspar J.: Radial-distribution studies, high-pressure x-ray diffraction studies; Crystallography Section, Inorganic Materials Division
 Author: 5.7, 5.8
Plumb, Harmon H.: Ph.D. Northwestern University, 1954; low-temperature thermometry; Cryogenic Physics Section, Heat Division
Poland, Duncan E.: Ph.D. University of Wisconsin, 1963; physical chemistry and transport properties of solids; Solid State Physics Section, Atomic Physics Division
 Author: 4.4
Pollack, Gerald L.: Ph.D. California Institute of Technology, 1962; low-temperature physics; Crystal Chemistry Section, Inorganic Materials Division
 Author: 5.13

Pontius, Paul E.: Accurate measurements of mass volume and density; Chief, Mass and Volume Section, Metrology Division

Proctor, Thomas M.: Solid state physics; Sound Section, Mechanics Division Author: 4.18

Raspberry, Stanley D.: Spectrographic analysis; Spectrochemical Analysis Section, Analytical Chemistry Division Author: 3.9

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

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

Roberts, D. Ellis: Crystal growth; Solid State Physics Section, Atomic Physics Division Author: 2.9

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

Ross, Gaylon S.: Nucleation, crystal growth; Polymers Division Author: 2.14, 2.15

Roth, Robert S.: Ph.D. University of Illinois, 1951; x-ray diffraction studies, phase equilibria; Crystallography Section, Inorganic Materials Division Author: 5.6, 5.15

Rubin, Robert J.: Ph.D. Cornell University, 1951; theoretical chemical physics; Heat Division

Rubin, Sherwin: Electronic engineering; Engineering Electronics Section, Instrumentation Division Author: 4.6

Ruff, Arthur W., Jr.: Ph.D. University of Maryland, 1963; dislocations and etch pits; Chief, Lattice Defects and Microstructures Section, Metallurgy Division Author: 3.3, 3.4

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

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

Schafft, Harry A.: Semiconductor devices and breakdown phenomena; Electron Devices Section, Instrumentation Division Author: 3.10

Schneider, Samuel J.: Phase equilibria of oxide systems and melting-point standards; Crystallography Section, Inorganic Materials Division Author: 4.14

Schooley, James F.: Ph.D. University of California, 1961; crystal growth for low-temperature paramagnetic studies; Cryogenic Physics Section, Heat Division Author: 4.21

Schoonover, Irl C.: Ph.D. Princeton University, 1933; research administration; N. B. S. Deputy Director

Schoonover, R. M.: Density determination; Mass and Volume Section, Metrology Division Author: 4.19

Scribner, Boudon F.: Analytical applications of optical and x-ray spectroscopy; Chief, Spectrochemical Analysis Section, Analytical Chemistry Division Author: 3.9

Simmons, John A.: Ph.D. University of California, 1961; mathematical physics; Metal Physics Section, Metallurgy Division Author: 2.20

Spinner, Sam: Elastic properties of inorganic solids; Physical Properties Section, Inorganic Materials Division Author: 3.13, 4.11

Sober, A. J.: Inorganic chemistry; Crystal Chemistry Section, Inorganic Materials Division Author: 2.13

Streever, Ralph L.: Ph.D. Rutgers University, 1960; nuclear magnetic resonance; Magnetic Measurements Section, Electricity Division Author: 4.13

Swanson, Howard E.: Physical chemistry, x-ray diffraction; Crystallography Section, Inorganic Materials Division Author: 5.1

Swartzendruber, Lydon J.: Solid state physics; Electron Devices Section, Instrumentation Division Author: 3.10

Termini, Dominic J.: Nucleation and crystal growth; Analytical Chemistry Division

Thurber, Willis R.: Thermoelectricity; Solid State Physics Section, Atomic Physics Division Author: 4.4

Tighe, Nancy J.: Defect studies by electron microscopy of non-metallic crystals; Physical Properties Section, Inorganic Materials Division Author: 3.11

Torgesen, John L.: Ph.D. Columbia University, 1942; crystal growth from solutions, impurity retentions, crystal properties; Crystal Chemistry Section, Inorganic Materials Division. Author: 2.7, 2.12, 2.13

Trisch, Ronald C.: Nuclear magnetic resonance; Solid State Physics Section, Atomic Physics Division

Vieth, D.: Electronprobe microanalysis; Lattice Defects and Microstructures Section, Metallurgy Division Author: 5.17

Wachtman, John B., Jr.: Ph.D. University of Maryland, 1961; mechanical and electrical properties of crystals; Chief, Physical Properties Section, Inorganic Materials Division Author: 3.13, 4.11, 4.2

Wagman, Donald D.: Thermochemistry and chemical thermodynamics; Chief, Thermochemistry Section, Physical Chemistry Division

Wasilik, John H.: Ph.D. Catholic University, 1956; dielectric constant and losses, ultrasonics; Solid State Physics Section, Atomic Physics Division Author: 4.7

Weeks, James J.: Measurements of dielectric properties of polymers, crystallization and melting of polymers; Dielectric Section, Electricity Division Author: 2.16

Weir, Charles E.: Infrared spectroscopy and high-pressure physics; Crystallography Section, Inorganic Materials Division. Author: 5.8, 5.9

Wiederhorn, Sheldon M.: Ph.D. University of Illinois, 1960; optical properties of high pressure, fracture of solids; Physical Properties Section, Inorganic Materials Division Author: 4.12

Will, Richard S.: Electron-field emission; Electron Physics Division

Williams, Robert S.: Solid state; Crystal Chemistry Section, Inorganic Materials Division

Winogradoff, N.: Ph.D. University of Edinburgh, 1945; interaction of radiation with matter; Electron Devices Section, Instrumentation Division Author: 3.10

Yakowitz, H.: X-ray microdiffraction, electronprobe microanalysis; Lattice Defects and Microstructures Section, Metallurgy Division Author: 5.17

Yolken, Howard T.: Growth of oxide films; Corrosion Section, Metallurgy Division

Young, John D.: Crystal growth by electrodeposition; Electrolysis and Metal Deposition Section, Metallurgy Division

Participants at the Boulder Laboratories

Arp, Vincent D.: Ph.D. University of California, 1959; superconductivity; Cryogenic Properties of Solids Section, Cryogenic Engineering Laboratories Author: 4.20

Bamberger, Edwin C.: Dielectric measurements; Radio and Microwave Materials Section, Radio Standards Physics Division

Bussey, Howard E.: Ph.D. University of Colorado, 1964; magnetism and ferrites; Radio and Microwave Materials Section, Radio Standards Physics Division Author: 4.10

Cook, Alan R.: Physical instrumentation; Radio and Microwave Materials Section, Radio Standards Physics Division Author: 3.12

Dalke, John L.: 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

Guntner, Charles S.: Imperfections, flow and fracture, phase transformations; Properties of Materials Section, Cryogenics Engineering Laboratories

Jefferson, Clinton F.: Ph.D. University of Michigan, 1959; solid solution for ferrimagnetic characterists; Radio and Microwave Materials Section, Radio Standards Physics Division

Mahler, Robert J.: Ph.D. University of Colorado, 1963; solid state physics; Radio and Microwave Materials Section, Radio Standards Physics Division Author: 3.12

Matarrese, Lawrence M.: Ph.D. University of Chicago, 1954; solid state physics, EPR resonance spectroscopy related to solid state mechanisms; Radio and Microwave Materials Section, Radio Standards Physics Division Author: 3.12

Peterson, Robert L.: Ph.D. Lehigh University, 1959; theoretical physics; Radio and Microwave Materials Section, Radio Standards Physics Division Author: 3.12

Powell, Robert L.: Thermal and electrical conduction of metals at low temperatures; Properties of Materials Section, Cryogenic Engineering Laboratory

Reed, Richard P.: Imperfections, flow and fracture, phase transformations; Properties of Materials Section, Cryogenic Engineering Laboratory

Risley, Alan S.: Magnetism and ferrites; Radio and Microwave Materials Section, Radio Standards Physics Division Author: 4.10

Wells, Joseph S.: Ph.D. University of Colorado, 1964; microwave physics, solid state physics relating to ENDOR and NMR; Radio and Microwave Materials Section, Radio Standards Physics Division Author: 3.12

Winder, Dale R.: Ph.D. Case Institute of Technology, 1957; solid state physics; Radio and Microwave Materials Section, Radio Standards Physics Division

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