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SOLID STATE DIVISION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING AUGUST 30, 1956

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**ORNL-2188**

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**SOLID STATE DIVISION SEMIANNUAL PROGRESS REPORT**

**FOR PERIOD ENDING AUGUST 30, 1956**

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SOLID STATE DIVISION

SEMIANNUAL PROGRESS REPORT

For Period Ending August 30, 1956

D. S. Billington, Director
J. H. Crawford, Jr., Assistant Director

DATE ISSUED

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J. B. Trice, A Flux Depression Experiment in the MTR, ORNL-2164 (Sept. 1956).


SOLID STATE REACTIONS

Effects of Gamma Irradiation on Germanium. — The removal rate of conduction electrons in germanium is increased during fast-neutron irradiation at liquid-nitrogen temperature over that at room temperature, and subsequent warmup curves reveal thermally unstable trapping levels. Similar experiments utilizing gamma rays reveal no increase in removal rate and no evidence of thermal instability, but the photoconductivity at liquid-nitrogen temperature after irradiation is increased by several orders of magnitude.

Antimony-Beryllium Neutron-Source Irradiation of Germanium. — The extreme sensitivity of high-purity germanium to lattice damage from fast particles or gamma rays indicates that such material might be employed for flux monitoring of various radioactive sources. Preliminary measurements have been made utilizing the monoenergetic fast neutrons emitted by an antimony-beryllium source, but the accompanying gamma-ray intensity exceeds the fast-neutron intensity in this particular source. Other radioactive sources that do not radiate a variety of intensities are being examined.

The Magnetic Susceptibility of Silicon. — The magnetic-susceptibility—temperature curves of an additional number of n- and p-type silicon samples have been determined, but lack of Hall and conductivity curves for the samples prevents complete interpretation of the data. At lower temperatures, in that portion of the total susceptiblity attributed to the carriers in the n-type material, the appearance of an effect resembling paramagnetism is considered to be due to the freezing out of carriers. The susceptibility contribution of the holes in the p-type samples was found to be paramagnetic through the temperature range studied — a result which could be attributed either to the freezing-out effect or to a heavy effective mass for holes. On the basis of a published Hall curve for similar samples, the freezing-out effect is expected to be dominant; and it is concluded that frozen-out holes are paramagnetic in the concentration range studied. On the basis of the Hall data, the Hall curves are interpreted to indicate that \( \tau _{c} \) cannot be greater than 3.

Magnetic Susceptibility of Irradiated Silicon. — Holes trapped out as a result of fast-neutron bombardment disappeared magnetically, as did the trapped electrons in irradiated germanium. The carrier contribution in the n-type silicon sample changed from diamagnetic to paramagnetic upon irradiation — a result which cannot be interpreted conclusively because Hall or conductivity curves for the irradiated specimen were not available. Irradiation of near-intrinsic silicon increases its diamagnetic susceptibility at room temperature and alters the temperature dependence of the susceptibility slightly. It is postulated that this alteration of temperature dependence in the irradiated intrinsic specimen results from a radiation-induced change in the Van Vleck paramagnetism, a concept which was originally invoked by Krumhansl and Brooks to explain the temperature dependence of the susceptibility of pure unirradiated silicon and germanium.

The Magnetic Susceptibility of Barium Titanate. — The curve of the magnetic susceptibility as a function of temperature for a crystal of barium titanate has been determined in the temperature range 67 to 405°C. The room-temperature value of the specific susceptibility was found to be \(-8.47 \times 10^{8}\) cgs. The four phase transitions were visible as discontinuities in the curve. The over-all temperature dependence was equivalent to approximately \(5 \times 10^{19}\) s-like paramagnetic centers per cubic centimeter. Theoretical analysis of the data is only partially complete.

The Effect of Radiation on the Electrochemical Behavior of Germanium Single Crystals. — The effect of fast-neutron bombardment on the electrode potential of germanium has been investigated. Although the potential of the cell Ge(0.1 N KOH) saturated calomel is not highly reproducible and drifts with time, the change of \(-0.02\) V produced by fast-neutron bombardment is considerably greater than the uncertainty of the cell potential. The effect of annealing was also studied, and it was found that the change in potential recovered in the same range as that in which the etching effect annealed.

Effects of Radiation on Electronic Components. — A model is proposed to explain why transistors of
different types of construction show various sensitivities to surface conditions.

Annealing due to the presence of the electric field at the barrier of a semiconductor diode is noted.

Characteristic curves have been obtained for a Philco surface-barrier transistor before and after a series of irradiations in hole 51N of the ORNL Graphite Reactor. Although the \( I_{c0} \) characteristic showed considerable change, the \( I_{c} \) family of curves remained essentially unchanged after an irradiation of \( 9.96 \times 10^{12} \text{ neut}/\text{sec} \).

Measurements of a silicon junction diode irradiated without interruption do not show the anomalous behavior that was observed in previous experiments in which the exposures were interrupted.

The Effect of Bombardment on Optical Absorption. — Preliminary studies of the optical-absorption spectra of fast-neutron-bombarded specimens of high-purity germanium reveal that, in addition to inducing the wavelength-independent absorption beyond the fundamental absorption edge, \( \sim 1.6 \mu \) (previously reported), irradiation has a marked effect on the onset of fundamental absorption as well. The rate of increase of absorption coefficient with decreasing wavelength is markedly increased after fast-neutron bombardment.

The Optical-Absorption Behavior of Irradiated Solids. — Preliminary results on the fast-neutron irradiation of synthetic and natural quartz and of three different vitreous-silica materials (including Corning high-purity silica) are presented. On the basis of these results, it appears that the coloration in these materials is due to the formation of free radicals. The existence of the 2570 Å band has been demonstrated in Corning silica irradiated with Co60 gammas. In addition to the two previously identified absorption bands (2570 Å and 2120 Å), an increase in absorption near the lower limit of the Cary model 14 instrument indicates the buildup of either an absorption band below 1850 Å or a general increase in the fundamental absorption.

ENGINEERING PROPERTIES

Infrared Spectra of Plastics and Elastomers After Irradiation. — Measurements have been continued on irradiated polymer specimens exposed to air and have shown that oxidation progresses for periods as long as 200 days. The measurements proved that after irradiation in vacuum and subsequent exposure to oxygen all the materials examined experienced oxidation.

In order to determine the concentrations of the molecular groups observed in the infrared spectra, absorption coefficients of these groups are being measured on standards made up of simple compounds. The determination of the densities and thicknesses of the specimens also presents some problems, and these measurements are being carried out.

Effects of High-Energy Radiation on Polymers. — Preparations were made for the study of the effect of radiation on the molecular weight of two common vinyl polymers (polystyrene and polymethyl methacrylate) which differ widely in their resistance to radiation. In order to determine the average molecular weight of the commercial materials used as samples, viscosity measurements have been made on solutions of various concentrations. By means of a precipitation technique, the commercial plastics have been fractionated into samples of various average molecular weights.

A new elastomer, polyfluorobutyl acrylate, has been irradiated and subjected to engineering tests in continuation of the program of evaluation of plastics and elastomers for technical applications.

Radiation Stability of Ceramic Materials. — Density changes were measured for a group of ceramic materials for which the effects of radiation on other properties have already been studied. The apparatus for measuring elastic constants and internal friction is being modified so as to permit measurements from -100 to 500°C. A calorimeter is being built for measuring stored energy.

RADIATION METALLURGY

HRP Radiation Metallurgy. — Subsize Izod impact specimens of four irradiated steels have been tested. The results presented show increases in impact-energy transition temperatures and decreases in “ductile” fracture energy.

Tensile data have shown several unusual characteristics of irradiated irons and steels. With sufficient irradiation, the elongation before necking decreases to the order of 1%; and in irradiated high-purity irons, the ductility is strongly dependent on the strain rate. Fine-grained steels do not show this effect.
Ductility Measurements of Nickel and Some High-Nickel Alloys. — For the purpose of determining the existence of any ductility anomalies, a series of tensile tests were run on nickel, Nichrome V, and Inconel at two strain rates and at temperatures ranging from 800 to 1600°F. Ductility minimums were observed in Nichrome V and in nickel but none in Inconel.

CHEMICAL EFFECTS OF NUCLEAR REACTIONS

The Reaction of Boric Acid with Some Pyridine Bases. — Orthoboric acid, $\text{H}_3\text{BO}_3$, has been found to react readily with pyridine and with several of its homologs. The crystalline reaction products appear to have orthorhombic symmetry and are probably addition compounds of metaboric acid, HBO$_2$.

REACTOR EXPERIMENTS

Effect of Radiation on Analysis of Chromium, Iron, and Nickel. — Preliminary results from tests pertaining to the effect of radiation on the analytical measurement of chromium indicate a possible increase in the amount of chromium apparently present.

Holdup of Fission Gases by Charcoal Traps. — Studies are being conducted for the purpose of determining the effect of trap geometry on the holdup of fission gases by charcoal.

LOW-TEMPERATURE METAL PHYSICS

Techniques and Equipment Utilized in Low-Temperature Reactor Irradiations. — The construction details of a cryostat located in the ORNL Graphite Reactor and the associated bombardment techniques at 15°K are reported. A method for measuring the stored energy of samples bombarded in the cryostat and, in addition, a method for pulse-annealing specimens bombarded at low temperatures are described. Mention is also made of the hazards which are encountered in low-temperature bombardments and which are attributed to the apparent formation of ozone.

Mechanisms of Annealing in Neutron-Irradiated Metals. — In an effort to understand the effects of radiation on the properties of metals, the information available from low-temperature irradiations has been reviewed. Particular attention has been devoted to the annealing kinetics of those processes which change the electrical resistivity in the temperature range 30 to 60°K. The suggestion has been made that a defect called the crowdon plays an important role in this annealing. The crowdon may also play an important role in the properties of metals at room temperature and above.

Low-Temperature Deformation of Copper Single Crystals. — Particular attention is being placed on the anomalous behavior of copper when deformed at low temperature. It has been shown that twinning is one process which occurs at this temperature. Another process which occurs has been labeled discontinuous slip. This latter process is not understood. The anomalous fracture of copper at 4,2°K is also discussed. It is pointed out that in certain instances the theoretical strength of copper is reached before fracture occurs.

The X-Ray Determination of Double Deformation Twins in Copper. — A single crystal of copper deformed by tensile extension at 4,2°K resulted in the formation of two separate and distinct (111) twin relationships. These relations were unambiguously determined by a unique x-ray technique which employs a type of stereographic projection. The method and results are presented in detail.

Operation of Dual X-Ray Tubes from a Single High-Voltage Power Supply. — The simultaneous operation of two x-ray diffraction tubes from the single high-voltage supply of the water-cooled North American Philips unit is described. The system is operated with full-wave rectification under optimum power ratings and with the two diffraction tubes separated by 5 ft on adjoining tables.

In-Pile Measurements at Low Temperature of Young's Modulus and Internal Friction. — Measurements of Young's modulus and the internal friction of a copper single crystal in the presence of neutron irradiation at 20°K show that there is a dislocation contribution which is eliminated by the bombardment. It is also shown that there is an "annealing knee," which becomes active at about 35°K. If use is made of previous room-temperature data, arguments in favor of interstitial motion at low temperature can be advanced.

SPECIAL PROJECTS

The Precipitation-Hardening Reaction in Nickel-Beryllium. — The precipitation-hardening reaction in a supersaturated solution of beryllium in nickel
was studied by measuring the Curie temperature, the hardness, and the resistivity of a number of specimens which were heat-treated at different temperatures. From the measurements it appears that the precipitation process progresses in three stages, which are designated as nucleation, growth, and overaging. The activation energy for the second, or growth, stage is 2.55 ev.

Specimens irradiated for one month in the ORNL Graphite Reactor at room temperature were also heat-treated in order to compare them with control specimens. The irradiated specimens seemed to show a faster reaction rate during the first, or nucleation, stage, but otherwise no differences in the main precipitation process appeared.

**Effect of Neutron Radiation on an Aluminum-Silver Precipitate Alloy.** Two originally identical samples of 80 wt % Al–20 wt % Ag have been heat-treated for a total of 60 hr at 100°C; one sample had been irradiated to $10^{19}$ neutrons and the other to only $10^{18}$ neutrons. Small-angle x-ray scattering patterns were taken at various intervals during the heat treatment, and the slopes of the log-intensity vs angle-squared curves are shown as a function of time at temperature. The data confirm earlier less refined measurements which showed that after irradiation there is a retardation of precipitate growth during heat treatment.

**Small-Angle X-Ray Scattering Technique.** It has been shown that the Ross filtering technique can be applied to great advantage in obtaining small-angle x-ray scattering from a few precipitate alloys in which the matrix is more dense than the precipitate.

Some preliminary measurements of small-angle x-ray scattering have been made with the alloy nickel-beryllium.

**Paramagnetic Resonance of Impurities in MgO Single Crystals.** On the basis of the hyperfine interaction constant, nuclear spin, satellite structure, and g value, two impurities, manganese and vanadium, have been identified in an MgO single crystal. There are other lines present which have not been identified. The g value of one of these lines is the same as that of a line identified by one worker as being due to iron and by another worker as being due to excess oxygen, that is, O²⁻ ion.

**Paramagnetic Resonances in Irradiated MgO Single Crystals.** Two primary effects of neutron irradiation on MgO single crystals are the production of paramagnetic centers and the elimination of centers associated with impurities. The induced paramagnetic resonances have a g value of $2.0022 \pm 0.0004$. The resonance is not a single one, since there is a complex satellite structure associated with it. The structure of a resonance expected from an f center in MgO was postulated, and the calculated line was compared with the observed line; the agreement was not good. No explanation for the elimination of the impurity lines has been found.

**Paramagnetic Resonance in Irradiated Crystaline Quartz.** The paramagnetic-resonance data for neutron-irradiated crystalline quartz have been analyzed in detail. The interpretation suggests that the defect producing the resonance is an interstitial atom or complex associated with two silicon atoms. The electron giving rise to the resonance spends only a small fraction of its time on these associated silicons.

**Neutron-Flux Measurements.** A boron shield was tested for the attenuation of a neutron flux at 135 and 340 ev. A strontium-beryllium photo-neutron source was found to be unsatisfactory for studies of the irradiation effects of monoenergetic neutrons.

**The Quenching-In of Lattice Defects in Gold-Cadmium.** The energy of formation, $\epsilon_F$, and the activation energy for motion, $\epsilon_M$, of quenched-in defects were determined from resistivity measurements. In addition, the time of holding at the quench temperature was varied and found to have no effect upon the amount of quenched-in resistivity. Also, $\epsilon_F$ and $\epsilon_M$ were determined from resistivity measurements on a sample for which these parameters had previously been determined by measurement of the changes in density and dimension upon quenching. The results based on resistivity, density, and dimensional measurements were found to be in agreement. Based on theoretical calculations, an estimate is made of the concentration of quenched-in vacancies, as deduced from the changes in resistivity and density. Measurements were made of the rate of cooling during the quenching operation, and the rate was found to be of the order of $10^4$°C/sec. This value for the quenching rate is found to be consistent with the observed activation energy of motion, annealing times, and temperatures.

**X-Ray Examination of Miscellaneous Irradiated Specimens.** Molybdenum wire showed no change in its x-ray pattern after irradiation.
Asbestos which had been in the ORNL Graphite Reactor for 12 years showed a slight degree of disordering in its x-ray pattern but no optical changes from normal chrysotile.

Specimen Rotator for the Radiodiffractometer. — A specimen rotator has been added to the radiodiffractometer so that specimens exhibiting preferred orientation can be examined.

Thermal Conductivity of Irradiated Nonmetals at Low Temperatures. — The thermal conductivity of high-purity germanium single crystals has been measured at low temperatures before and after bombardment by fast neutrons. Bombardment causes a decrease in the thermal conductivity at the lowest temperatures (helium region), which does not anneal except by subsequent heat treatment at elevated temperatures (~400°C).

The decrease in the value of thermal conductivity at low temperatures after neutron bombardment has also been measured on single crystals of lithium fluoride and potassium chloride. A potassium chloride single crystal which was unannealed initially was shown to have been partially annealed by successive Co⁶⁰ gamma bombardments; the increase in thermal conductivity at low temperatures is considered as an index of annealing.
SOLID STATE REACTIONS

EFFECTS OF GAMMA IRRADIATION ON GERMANIUM


In the previous semiannual report\(^1\) experimental data were presented which indicated that energetic photons from a Co\(^{60}\) gamma source produce lattice defects in germanium; moreover, the defect states thus produced corresponded with those observed in neutron-irradiated specimens, and this was taken as an indication that interstitials and vacancies are uniformly produced throughout the specimen.

Low-temperature (\(\sim 100^\circ K\)), fast-neutron irradiation of \(n\)-type germanium increases the removal rate of conduction electrons by a factor of \(\sim 1.5\); and warmup curves, subsequent to irradiation, indicate the presence of two additional trapping levels that are thermally unstable.\(^2\) The removal rate of electrons from \(n\)-type germanium by gamma rays, however, does not appear to be enhanced by low-temperature (\(\sim 77^\circ K\)) irradiation. No evidence of any thermally unstable trapping mechanism has been indicated by subsequent warmup curves.

The primary result of gamma-ray irradiation at liquid-nitrogen temperature is to increase the photocconductivity of the sample at the irradiation temperature from an approximately zero amount beforehand to an amount almost several orders of magnitude greater after a fairly short irradiation. The dark conductivity (as determined by removal from the region of gamma flux), the gamma-source conductivity, and the conductivity under room-light or flashlight illumination represent three values of increased conductivity. As yet, no attempt to correlate exactly the change in photocconductivity with either light intensity or irradiation time has been completed.

ANTIMONY-BERYLLIUM NEUTRON-SOURCE IRRADIATION OF GERMANIUM


The removal rate of conduction electrons from high-purity \(n\)-type specimens of germanium by fast neutrons should be a sensitive function of the fast-neutron energy; hence, it is of interest to investigate the mechanism, since possible flux-monitoring applications are implied. Fast neutrons of known energy spectrum in the kilovolt range can be produced by impinging the hard gamma rays emitted by Sb\(^{124}\) on beryllium. High-level antimony-beryllium sources emitting \(\sim 10^7\) neutrons/sec are available from the Radioisotope Sales Department of the Operations Division of Oak Ridge National Laboratory.

A single-crystal high-purity \(n\)-type sample of germanium with an initial carrier concentration of \(\sim 2.1 \times 10^{12}\) electrons/cm\(^3\) has been exposed to an antimony-beryllium source with an estimated total \(nat\) of \(3 \times 10^{10}\) fast neutrons, but such an exposure also irradiates the same specimen with an estimated total flux of \(\sim 5 \times 10^{15}\) gamma rays. Since the cross section for the production of lattice defects by fast neutrons in germanium is only \(\sim 1000\) times as great as that for the production of similar defects by gamma rays, the decrease in carrier concentration observed in the specimen, which amounted to \(1 \times 10^{12}\) electrons/cm\(^3\), is believed to be due mostly to the gamma rays. Consequently, the above technique does not permit an identification of the carrier removal rate for the particular monoenergetic fast neutrons in question, but the extreme sensitivity of the high-purity germanium currently available does indicate that certain radioactive-decay sources emitting beta rays, gamma rays, or fast neutrons of sufficient quantity and energy can be employed to critically examine such processes as the binding energy between atoms and the irradiation energy required to produce individual and perhaps multiple defects.

THE MAGNETIC SUSCEPTIBILITY OF SILICON

D. K. Stevens  W. J. Sturm\(^3\)  J. H. Crawford, Jr.

The temperature dependences of the magnetic susceptibility of an additional number of samples of single-crystal silicon\(^4\) have been measured.


\(^3\)Currently employed at the Argonne National Laboratory, Chicago, Ill.

\(^4\)The samples measured were gifts of the Bell Telephone Laboratories and the General Electric Research Laboratories.
SOLID STATE PROGRESS REPORT

In a manner previously described,\textsuperscript{5} Faraday-type measurements were carried out on $\frac{1}{4}$-in. cubes suspended on a length of 0.001-in.-dia molybdenum wire. Table 1 lists the room-temperature resistivity and the carrier concentration for each sample, as well as its doping agent; this information was furnished by the suppliers of the samples.

Figure 1 is a summary of the magnetic measurements on n-type silicon. Although sample No. 26-76-6 is p-type, it contains a concentration of carriers that is too small to make a measurable contribution to its total susceptibility and is considered representative of pure silicon. Based on arguments presented previously,\textsuperscript{5} the difference between the curve for this sample and that of any other sample is expected to represent the susceptibilities of the carriers, free or frozen out, in the less pure sample.

A critical analysis of the data will have to await measurements as a function of temperature of the Hall constant and the conductivity of each specimen, since the precise manner in which the free-carrier concentrations of these samples change with temperature is not known. Measurement of these properties at just one temperature, namely, room temperature, would help resolve apparent contradictions between the room-temperature values of the susceptibilities and the stated free-carrier concentrations. For example, samples 743-1 and 743-2 are shown in Fig. 1 as a single curve because the magnetic data of each have the same temperature dependence within relative experimental error (±0.1%), and the average absolute values of the room-temperature susceptibilities differ by only 0.5% (within absolute experimental error), although in the opposite manner expected from the stated carrier concentrations. From the nominal ratio of free-carrier concentrations, a separation of the curves of the order of 5% is expected. On the other hand,


### TABLE 1. DATA PERTAINING TO MAGNETIC-SUSCEPTIBILITY MEASUREMENTS OF n-TYPE AND p-TYPE SILICON SPECIMENS

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Doping Agent</th>
<th>Resistivity\textsuperscript{a} (ohm-cm)</th>
<th>Carrier Concentration\textsuperscript{a,b} (cm\textsuperscript{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>26-76-7</td>
<td>Arsenic</td>
<td>0.0024–0.0035</td>
<td>$3 \times 10^{19}$</td>
</tr>
<tr>
<td>743-1</td>
<td>Arsenic</td>
<td>0.0138</td>
<td>$2.5 \times 10^{18}$</td>
</tr>
<tr>
<td>743-2</td>
<td>Arsenic</td>
<td>0.0109</td>
<td>$4 \times 10^{18}$</td>
</tr>
<tr>
<td>RR-174</td>
<td>Phosphorus</td>
<td>0.007</td>
<td>$2 \times 10^{18}$</td>
</tr>
<tr>
<td>VI-1047B</td>
<td>Arsenic</td>
<td>0.015</td>
<td>$3 \times 10^{18}$</td>
</tr>
<tr>
<td>RR-176</td>
<td>Phosphorus</td>
<td>0.023</td>
<td>$7 \times 10^{17}$</td>
</tr>
<tr>
<td>RR-176-F</td>
<td>Phosphorus</td>
<td>0.075</td>
<td>$1 \times 10^{17}$</td>
</tr>
<tr>
<td>V-1162</td>
<td>Boron</td>
<td>0.002</td>
<td>$2.3 \times 10^{18}$</td>
</tr>
<tr>
<td>C-Si-228</td>
<td>Boron</td>
<td>0.028</td>
<td>$1.7 \times 10^{18}$</td>
</tr>
<tr>
<td>C-Si-253</td>
<td>Boron</td>
<td>0.21</td>
<td>$1.3 \times 10^{17}$</td>
</tr>
<tr>
<td>26-76-6\textsuperscript{c}</td>
<td></td>
<td>35</td>
<td>$4.1 \times 10^{14}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Resistivities and carrier concentrations at room temperature.

\textsuperscript{b}Carrier concentrations: ±20% for n-type, ±40% for p-type.

\textsuperscript{c}In the previous report of this series, ORNL-2051, this sample was designated as 35-P.
Fig. 1. Diamagnetic Susceptibility vs Temperature Curves for n-Type Silicon.

In consideration of the stated possible error, if the actual values of the carrier concentrations are at the most favorable extremes, that is, $3.0 \times 10^{18}/\text{cm}^3$ for 743-1 and $3.2 \times 10^{18}/\text{cm}^3$ for 743-2 (roughly the same concentration claimed for sample VI-1407B), a difference in the room-temperature susceptibilities of only 0.5% is in the proper range. The position and curvature of the susceptibility plot of sample VI-1407B do not fit into this scheme of rationalization, however.

In the temperature range studied, the room-temperature value and temperature dependence of the susceptibility of sample RR-176-F are similar to those of the "pure" sample 26-76-6. In view of the number of carriers involved, this result is not surprising, although differences should become apparent at lower temperatures.

The data obtained on sample RR-176 were discussed in the last report in this series. Although its temperature dependence can be rationalized on the basis of freezing-out effects (to be discussed below), its absolute position remains anomalous. In each case, the x-ray density was used to determine the absolute susceptibility because in those few cases where the density was measured by means of a buoyancy technique the values so obtained agreed with the x-ray density. If there is a large concentration of voids present in any sample, the experimentally determined value of the susceptibility would result in an error in the ratio of the true density to the x-ray density.

The appearance of a paramagnetic contribution at the lower temperature ranges in samples 743-1 and 743-2 and VI-1407B is presumed to be due to the "freezing out" or to deionization of electrons from the conduction band to donor sites. When this process takes place (on the assumption that the donor sites are so few in number that overlap does not occur either with the edge of the conduction band or with each other), the electron will lose its Landau diamagnetism and retain its spin paramagnetism. Morin and Maita in their studies of the electrical properties of silicon have shown that the "freezing out" effect can take place in this temperature range in n-type silicon having a net impurity concentration as high as $2.2 \times 10^{18}/\text{cm}^3$. Thus, in silicon samples, which are electron conductors having impurity concentrations of this order or less and in which no overlap occurs, the contribution of the carriers to the total susceptibility might be expected to change from diamagnetic to paramagnetic as the temperatures are lowered through the range of this transition. (Where impurity concentrations are high enough for impurity bands to occur which do not fuse with the conduction band, the carrier contribution may remain diamagnetic, depending upon the effective masses of the carriers when in these bands.) Van Itterbeek et al. have observed diamagnetic-paramagnetic transitions in germanium at much lower temperatures.

Morin and Maita have shown that the free-carrier concentration in n- and p-type silicon

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remains independent of temperature at concentrations above $10^{19}$/cm$^3$. Thus, the qualitative magnetic behavior of sample 26-76-7 would be expected to differ from that of 743-1 and 743-2 and VI-1407B, since the carrier concentration of this sample is reported to be $3 \times 10^{19}$/cm$^3$.

Comparison of the room-temperature susceptibility and the slope of the susceptibility temperature curve of sample RR-174 with the data from the curves of the other samples indicates that the carrier concentration of this former sample is indeed of the order of $10^{18}$/cm$^3$, as against $10^{19}$/cm$^3$. The apparent failure of the paramagnetic component to become dominant at the lower temperatures, as it did in the other less impure samples, suggests that this sample may be heavily compensated. If the density of donor sites is large enough for a high degree of overlap to occur, a simple transition from diamagnetic to paramagnetic character would not be expected to necessarily occur. One factor of importance in this case would be the effective masses of carriers when in the impurity bands, and another factor would be the degree of fusion between the impurity and conduction bands.

The data obtained on $p$-type samples are summarized in Fig. 2. As with the $n$-type data, a critical analysis must await Hall and conductivity measurements as a function of temperature. The room-temperature points appear to be more consistent with those expected from the reported carrier concentrations than were those for the $n$-type samples. Also, it can be seen that the over-all contribution of holes in silicon is paramagnetic, even in that temperature range where the holes are expected to be essentially free. Since a high rate of freezing out of holes in this temperature range, as well as the suitably averaged value of the effective mass of holes, can shift the temperature dependence of the carrier susceptibility from negative to positive, only tentative conclusions can be drawn, concerning the averaged hole effective mass in silicon, from the susceptibility data alone. However, by estimating the freezing-out rate from the data of Morin and Maita, and the data of Carlson, it was determined that the value of $J^2$, the square of the reciprocal mass-ratio tensor for motion of holes in a magnetic

\[ J^2 = \frac{m_e^*}{m_h^*} \]

field, calculated from the magnetic data, could not exceed 3.

Plotting the difference between the curve of sample 26-76-6 and that of any of the less pure $p$-type samples against reciprocal absolute temperature yields curves having a long straight-line segment at the higher values of reciprocal temperature. On the assumption that this portion of the curve represents the simple Curie dependence of a paramagnetic center having $s$-like character, the number of such centers can be calculated from the slope. The values determined in this manner are $2.76 \times 10^{18}$, $2.28 \times 10^{18}$, and $3 \times 10^{17}$/cm$^3$, respectively, for the samples reported to have $2.3 \times 10^{18}$, $1.7 \times 10^{18}$, and $1.3 \times 10^{17}$/cm$^3$ ($\pm 40\%$) free holes at room temperature. The agreement must be considered fortuitous, considering (1) the probability of overlap, (2) the probability of impurity-band formation, and (3) that only approximately $5\%$ of the holes in a sample having an impurity concentration of the order of $2 \times 10^{18}$/cm$^3$ would have frozen out upon reducing the temperature from 300 to 80°K, according to the data of Carlson.

Fig. 2. Diamagnetic Susceptibility vs Temperature Curves for $p$-Type Silicon.
MAGNETIC SUSCEPTIBILITY OF IRRADIATED SILICON

D. K. Stevens J. W. Cleland

Three samples of silicon, one high-resistivity p-type, one low-resistivity p-type and one low-resistivity n-type, were irradiated in hole 51 of the ORNL Graphite Reactor for a total estimated irradiation of $1.7 \times 10^{18} nvt_f$. Previously, it had been shown that both electrons and holes in silicon are trapped with nearly equal efficiency by disorder introduced by fast-neutron bombardment. The level of bombardment was chosen so that, on the basis of the stated carrier concentrations, all the carriers in the low-resistivity samples would be expected to be trapped out. No Hall or conductivity measurements were carried out before or after bombardment. Unfortunately, after this bombardment was completed, other n-type silicon became available which indicated that the n-type specimen chosen for bombardment, RR-174, is apparently atypical of n-type material (see the previous section of this report). The cubes irradiated were not measured before irradiation, but they were cut out of the same ingot wafers from which the unirradiated cubes were taken.

The results of magnetic-susceptibility measurements on the irradiated and unirradiated companion cubes are shown in Fig. 3. The following general observations are immediately apparent.

Relative to the unirradiated "pure" specimen, 26-76-6, (1) the paramagnetism of the p-type sample is reduced by fast-neutron bombardment, (2) the diamagnetism of the n-type sample is lost and the sample becomes paramagnetic, and (3) the diamagnetic susceptibility of the "pure" sample is increased approximately 0.5% at room temperature — its temperature dependence remains the same at room temperature but is altered at lower temperatures.

Based on the slopes of the low-temperature sections of Curie plots that are generated by subtraction of the curves of the p-type samples from the curves of the "pure" samples (unirradiated from unirradiated and irradiated from irradiated), the number of s-like paramagnetic centers has been found to reduce from $2.76 \times 10^{18}$ to $1.1 \times 10^{17}/\text{cm}^3$. When the holes are trapped out

Fig. 3. Diamagnetic Susceptibility vs Temperature Curves for Fast-Neutron-Bombarded n- and p-Type Silicon. The irradiated samples were exposed to an $nvt_f \approx 2 \times 10^{18}$.


electrically by radiation-introduced disorder, magnetic trapping occurs simultaneously — a result similar to that found for trapped conduction electrons in irradiated germanium. In spite of the large capture cross section of boron, neutron capture and conversion would not explain the results observed for boron-doped p-type silicon.

If the p-type data are an indication of the number of traps introduced by this bombardment and if the trapping efficiency is the same for both types of carriers, then at least $2.65 \times 10^{18}$ electrons/cm$^3$ should have been removed from the conduction band of the irradiated n-type sample. The low-temperature slope of a Curie plot, generated by the difference between the curves for the irradiated n-type specimen and irradiated "pure" specimen, indicates that approximately $7 \times 10^{17}$ s-like paramagnetic centers per cubic centimeter are present in the n-type specimen after irradiation. If the possibility of interaction
between the paramagnetic centers which give rise
to the Curie-plot difference curves is neglected,
two explanations of the data are immediately
evident:

1. The electrons located in irradiation-intro-
duced traps are not paramagnetic (in much the
same manner as the irradiation-trapped holes in
silicon and electrons in germanium are not
paramagnetic). The $7 \times 10^{17}$ s-like paramagnetic
centers per cubic centimeter are conduction
electrons which, because of insufficient irra-
diation, are not located in irradiation-produced
traps but are frozen out.

2. The electrons located in irradiation-intro-
duced traps exhibit paramagnetic properties. This
paramagnetism is in part counterbalanced by the
temperature-dependent Landau diamagnetism of a
few conduction electrons which were not trapped
out. The apparent $7 \times 10^{17}$ s-like paramagnetic
centers per cubic centimeter are the "uncompen-
sated" trapped electrons.

The shape of the Curie plot of the difference
curve would be similar for each of the two possi-
bilities discussed above but would differ slightly
in absolute value. In the case of possibility 1,
at high temperatures most of the electrons would
be in the conduction band, with the result that the
total impurity contribution should be diamagnetic.
As the temperature is lowered and freezing out
takes place, the contribution should go through
zero and become paramagnetic. In the case of
possibility 2, the contribution should remain
either diamagnetic or paramagnetic throughout the
temperature range (unless the conduction electrons
become highly degenerate at low temperatures),
since no freezing out occurs.

The data favor possibility 2, since no freezing-
out effects were evident in the unirradiated
sample, and the Curie plot remained paramagnetic
throughout the temperature range. Hall and
conductivity data as a function of temperature
are needed in order to make conclusive statements.
Since the $n$-type sample appears to be magnetically
atypical of $n$-type silicon, care must be exercised in
extrapolating these specific results to the
general case.

Relative to the unirradiated curve for the "pure"
sample, 26-75-6, the curve for the irradiated
companion sample shows a 0.5% shift toward
increased diamagnetism in the room-temperature
range. The curves tend to converge at liquid-
nitrogen temperature, however. If, as has been
discussed, the proposal of Krumhansl and
Brooks is valid, namely, that Van Vleck para-
magnetism is responsible for the temperature
dependence of the susceptibility of pure germanium
and silicon, then a change in the absolute value
at any given temperature or an alteration of the
over-all temperature dependence due to irradiation-
produced disorder is not unexpected. The ex-
pression for the Van Vleck paramagnetism involving
only one excited state $j$ is given by

$$\chi_{\nu \nu} = \frac{2N}{\rho} \frac{|\langle j | \mu_z | 0 \rangle|^2}{\Delta},$$

where $N$ is the number of atoms per cubic centi-
meter, $\rho$ is the density, $\Delta$ is the energy separation
between the ground state and the excited state,
and $\langle j | \mu_z | 0 \rangle$ is the magnetic-moment matrix
element connecting the two states. The tempera-
ture dependence of this term arises through the
temperature dependence of $\Delta$. Bombardment-
produced disorder might be expected to alter the
selection rules governing the transitions and both
the value and temperature dependence of $\Delta$, since
similar effects have been observed optically.

Unfortunately, it is not possible to observe
directly similar changes in the lattice susceptibility
of germanium because of the masking effect of the
holes produced by the long-term bombardment of
intrinsic material. However, it is to be noted that
when a cube of $n$-type germanium was bombarded
until it possessed intrinsic properties, such
that the number of free electrons or holes was too
small to be seen magnetically, its susceptibility-
temperature curve was shifted, relative to pure
germanium, in the direction of increased dia-
magnetism at room temperature; and the curve
tended toward convergence with that of pure
germanium at low temperature. It must be re-
membered, however, that there were approximately
$7 \times 10^{17}$ electrons located in bombardment-

12J. W. Crawford, Jr., and D. K. Stevens, Solid State
Soc. 11, 117 (1966).
14C. Kittel, Introduction to Solid State Physics, p 354,
15T. A. Longo and D. Kleitman, Phys. Rev. 100,
1260 (1955).
Aug. 30, 1955, ORNL-1945, Fig. 25, p 29.
produced traps after the bombardment. Thus, while the observations are similar to those for bombarded near-intrinsic silicon, the analogy is not without complications.

Further irradiation studies are planned.

THE MAGNETIC SUSCEPTIBILITY
OF BARIUM TITANATE

D. K. Stevens        H. C. Schweinler
W. J. Sturm           E. Sonder

The magnetic susceptibility of a polydomain barium titanate crystal, approximately 0.010 in. thick and weighing 170 mg, has been measured as a function of temperature from 67 to 405°K. The platelike crystal was hexagonal in shape, approximately 20 mm long and 7 mm wide, and was suspended by a 0.002-in.-dia copper wire threaded through a hole drilled (with an air drill) through the crystal near one of the apexes on the long axis of the crystal. The sample was the largest of several ordered by M. C. Wittels of this laboratory from the Brush Development Laboratory of the Clevite Corporation. The crystal was reported to have been grown from high-purity barium titanate; that is, no impurities were intentionally added to aid in the development of the crystal. Subsequent to the magnetic measurements, x-ray orientation studies at room temperature by Wittels indicated that the [110] crystallographic axis coincided with the suspension axis and that the [001] axis was normal to the plane of the crystal. Upon initial excitation of the magnet, the sample was observed to align itself so that its plane was parallel to the direction of the field. Subsequently, the suspension was adjusted so that the sample remained parallel to the field direction, whether or not the magnet was excited. Before calibration with oxygen at room temperature and before relative measurements as a function of temperature were made, the suspension length was adjusted so that the greatest force was exerted on the sample by the field [the value of $H (\partial H/\partial z)$ integrated over the sample was at a maximum].

With the use of oxygen as a standard, the room-temperature susceptibility of the sample was determined at four values of the field (above 10,000 gauss in every case). Since the susceptibilities so determined showed no significant trend with field, it was concluded that the sample was free of ferromagnetic contaminants. No correction for the suspension was applied to the results, since this correction was estimated to be less than 0.5% at room temperature. The susceptibility of a piezo quartz crystal, which was similar in shape to the barium titanate crystal, was measured, using the same copper suspending wire as was used for the barium titanate, and was found to be temperature independent (as expected for quartz), and agreed in absolute value with values determined by employing other techniques. The specific susceptibility of the barium titanate at 293.8°K was found to be $(−8.47 \pm 0.05) \times 10^{-8}$ cgs-units. The susceptibility at 373°K, the temperature which is just below that of the high-temperature phase transition, was also found to be insensitive to field (fields were in excess of 10,000 gauss).

The results of the temperature measurements are shown in Fig. 4. The data obtained below room temperature were taken as the sample was cooled, while the data obtained above room temperature were measured as the sample was heated. The phase transition just below room temperature was traversed in both directions without significant differences appearing in the data. The two phase transitions below room temperature,¹⁷ trigonal to orthorhombic near 200°K and orthorhombic to tetragonal near 275°K, are clearly visible as shifts toward higher diamagnetism in going to the lower-temperature


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**Fig. 4. Diamagnetic Susceptibility vs Temperature Curve of a Twinned Crystal of Barium Titanate.**
crystal form; while the one transition above room temperature, tetragonal to cubic at 390°K, is less obvious. A Curie plot of the data yields three parallel straight lines for the three lower-temperature phases. The slopes of the curves are equivalent to the temperature dependence of the susceptibility of $\sim 5 \times 10^{19}$ paramagnetic centers per cubic centimeter, each center having a $\mu$ equal to 1. Thus, a paramagnetic-impurity concentration of $\frac{1}{3}\%$ could account for the observed temperature dependence. A chemical analysis of the sample is not available at this writing.

Theoretical analysis of the data is under way. An attempt was made to fit the data in the four crystallographic phases to an expression of the form $\chi = -A + B/T$. The method of least squares was used, and preliminary results are given in Table 2.

THE EFFECT OF RADIATION ON THE ELECTROCHEMICAL BEHAVIOR OF GERMANIUM SINGLE CRYSTALS

R. Chang

In the course of investigating the etching behavior of germanium single crystals, it was found that chemical attack by an etchant such as CP-4 is greater on reactor-irradiated specimens than on unirradiated specimens. This was observed in a good germanium single crystal. The difference in etching rate between the irradiated and the unirradiated material became undetectably small when the

density of etch pits in the material was high. Apparently the phenomenon is associated with a difference in the electrochemical behavior of the irradiated and unirradiated material. Electrode-potential measurements were used as a means of investigating the problem further. The germanium single crystal, about $6 \times 3 \times 1$ mm, oriented so that its large face was parallel to a (111) plane, was used as one electrode, with a normal calomel half cell as the other electrode. The cell potential was measured at room temperature by means of a type K-2 potentiometer and a galvanometer having a sensitivity of about $3 \times 10^{-9}$ amp/mm.

Several investigators have reported on the electrochemical behavior of germanium. The consensus of opinion is that the electrode potential of germanium in various electrolytes, both aqueous and nonaqueous, is not reproducible and that its reversibility is questionable. In order to check this point further, its electrode potential was measured in various aqueous electrolytes, in

$\chi = -A + B/T$

<table>
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<tr>
<th>Temperature Range (°K)</th>
<th>Crystal System</th>
<th>$A \times 10^8$</th>
<th>$B \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>66.5–184.2</td>
<td>Trigonal</td>
<td>9.35</td>
<td>414</td>
</tr>
<tr>
<td>201.5–273.7</td>
<td>Orthorhombic</td>
<td>9.28</td>
<td>415</td>
</tr>
<tr>
<td>280–373.8</td>
<td>Tetragonal</td>
<td>9.95</td>
<td>435</td>
</tr>
<tr>
<td>379.8–405</td>
<td>Cubic</td>
<td>9.46*</td>
<td>254*</td>
</tr>
</tbody>
</table>

*Based on 4 points only.

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18 Summer Participant from Rutgers University.
19 A freshly made solution of 20 parts concentrated nitric acid, 12 parts glacial acetic acid, 12 parts 50% hydrofluoric acid, and 5 parts bromine.

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20 R. Schorz et al., Z. anorg. u. allgem. Chem. 229, 146 (1936).
23 G. Fink and V. M. Dokras, J. Electrochem. Soc. 95, 80 (1949).
conjunction with a normal calomel electrode. It was found that the potential decreases as the pH (or increasing hydrogen-ion concentration) of the electrolyte decreases. For example, changing the normality of electrolyte (KOH) by 0.1 results in a decrease in the cell potential of about 0.060 v. If the cell reaction is reversible with respect to the hydrogen-ion or hydroxyl-ion concentration in the electrolyte, then decreasing the pH of the electrolyte from 13 to 12 will result in a decrease in the cell potential at room temperature (20°C) of 0.058 v, which agrees with the experimentally observed value of 0.060 v. Results similar to those mentioned above were obtained by Brattain and Garrett,27 who found that changing the pH of the electrolyte from 13 to 1 resulted in a decrease in the cell potential of about 0.700 v, which is also in agreement with the predicted theoretical value of 0.698 v. On the other hand, varying the concentration of germanium ions in a 0.1 N KOH aqueous solution by a large factor, from a small trace to 0.1 mole by the addition of GeO₂, produces only a small decrease in the observed cell potential, which can be explained by the fact that the pH of the electrolyte was observed to have decreased slightly as a result of the addition of GeO₂. Tentatively, it may be concluded that the germanium electrode is, to a certain extent, reversible with respect to the hydrogen-ion or hydroxyl-ion concentration but is not reversible with respect to the germanium-ion concentration in the electrolyte. When a freshly etched germanium electrode is dipped into an electrolyte and its electrode potential is measured immediately, in conjunction with a normal calomel electrode, the potential initially drifts rapidly and then approaches a steady state, with a small, more or less constant, drift. According to Young,28 this is the normal behavior of cell potentials involving the formation of anodic oxide films, the initial fast drift being due to the growth and stabilization of space charges and the final, slow but steady, drift being due to the growth of the anodic oxide film. It is therefore reasonable to believe that an oxide film is formed on the germanium electrode, the nature of the film depending on the hydrogen-ion or hydroxyl-ion concentration in the electrolyte, and the cell is actually the following: Ge, GeO₅ₓ|electrolyte|calomel. This conclusion is tentative. Further study is necessary in order to establish the true cell reaction.

During actual cell-potential measurements, the drift of potential with time is noted; and the value obtained by extrapolation of the slow steady drift to zero time is taken as the observed cell potential. The reproducibility of measurements is sensitive to the surface condition of the germanium electrode. Before a measurement is taken, the germanium electrode is etched in a freshly prepared CP-4 solution until gas bubbles are evolved profusely from the surface of the electrode. It is then washed in water and dried, and the cell-potential measurements are made without further delay.

Single-crystal germanium electrodes, in sets of three each, were irradiated in the reactor at approximately 20°C to various total fast-neutron fluxes; and their electrode potentials in 0.01 N KOH aqueous solution, referred to the normal calomel, were measured at room temperature. The readings from three independent runs for a given integrated fast-neutron flux were averaged. It is found that the potential from germanium electrodes exposed to fast neutrons is slightly larger than that from the unirradiated ones. The difference in potential between the cell

irradiated germanium | 0.01 N KOH | calomel

and the cell

unirradiated germanium | 0.01 N KOH | calomel

is plotted versus the total fast-neutron flux in Fig. 5 and shows a consistent difference of about 0.020 v, which tends to decrease slightly with increasing neutron flux. The trend, however, is too small to be conclusive.

Annealing of the reactor-irradiated germanium tends to restore its electrode potential to that of the unirradiated condition. Annealing was carried out in a thermostatically controlled oil bath. The irradiated germanium electrode was given accumulated anneals at a constant temperature. After each anneal, its potential, referred to the normal calomel, was measured at room temperature. A few experiments were performed. The results are shown in Fig. 6.

The data are not considered sufficiently accurate for an interpretation. It will be desirable to improve the accuracy of measurements under more

strictly controlled conditions, a few of which are suggested below:
1. The selection of germanium single crystals of the greatest perfection. (Single crystals of germanium containing 30 to 40 etch pits per square centimeter have been reported in the literature.\textsuperscript{29})
2. The measurement of electrode potentials of germanium surfaces of various distinct orientations.
3. Closer control of the cell temperature and the introduction of cell temperature as a variable.
4. The introduction of current density as a second variable.
5. The introduction of light intensity as a third variable.\textsuperscript{27}

**Fig. 5. Difference in Electrode Potentials of Reactor-Irradiated (at \(\sim 20^\circ\text{C}\)) and Unirradiated Germanium.**

**Fig. 6. Annealing of Reactor-Irradiated (at \(\sim 20^\circ\text{C}\)) Germanium – Cell Potential Studies.**

**EFFECTS OF RADIATION ON ELECTRONIC COMPONENTS**

J. C. Pigg \quad C. C. Robinson

**Proposed Mechanism for Low-Dosage Radiation Effects in Transistors**

Temporary and permanent changes have been observed to occur in the electrical properties of germanium barrier devices, such as rectifiers and transistors, when these devices are exposed to radiation fields. For a transistor both the slope of the saturation part of the collector characteristic and the magnitude of the collector current are observed to increase. Similar results are observed in the reverse characteristic of a diode. These changes occur at levels of exposure that are below those for which a measurable change in the bulk properties of the semiconductor would be expected. It has also been observed that this behavior is markedly dependent upon the general construction of the unit under consideration.

An npn-grown junction is relatively insensitive to the presence of a stabilizing grease. On the other hand, pnp-grown-junction units and many pnp-alloy-junction units are sensitive to the presence of such grease; that is, under irradiation they show considerably greater changes when such grease is present than when it is not present.

A schematic representation of these two types of construction is shown in Fig. 7. Since the surface of a piece of germanium is p type, the surface path between the collector and the emitter in an npn-grown-junction unit includes an npn circuit, regardless of whether the conduction path is considered to be across the barriers or across the surface.

Fig. 7. Schematic Diagram Illustrating Mechanism of Surface Leakage.

A pnp-grown-junction device permits a leakage channel, in the form of a p-type conduction path, in parallel with the path across the barriers. Hence, chemical attack on the surface of the material by the gamma-ray-produced decomposition products of the grease would increase the depth of the p-type layer across the junction region and would serve to decrease the resistance of the parallel path and, thereby, result in an increase in the saturation slope of the characteristic curve.

In the pnp-alloy-junction unit, the situation is similar to the pnp-grown junction, except that the sensitive region is a small annular volume around the collector button. Since the surface current is spreading in the collector region, the leakage current is controlled by the conductivity and the depth of the p-type layer in this region.

This picture is consistent with the data from gamma exposures at ORNL\textsuperscript{30} and with that currently being accumulated at General Electric\textsuperscript{31} and Boeing Aircraft.\textsuperscript{32}

Enhanced Diffusion of Interstitials by an Electric Field

When germanium is bombarded by high-energy neutrons, the recoils from the neutron-atom collision and from secondary collisions of the original atom as it travels through the lattice result in the formation of lattice vacancies and interstitial atoms. Since the germanium lattice is fairly open, the interstitial atoms can diffuse readily through the crystal.

Because of the high dielectric constant of germanium (\(\sim 16\)), the interstitial atoms are normally ionized; and, hence, their diffusion through the crystal should be influenced by an electric field. Electric fields of the order of 1000 \(\text{v/cm}^3\) are present in the barrier region of a diode, and the conductivity of the diode is extremely sensitive to changes in the carrier concentration in the region of the barrier.

A 1N38-A point-contact germanium rectifier was inserted for 5 min in hole 51N of the ORNL Graphite Reactor. After removal from the reactor, the rectifier was biased in the forward direction at 0.7 \(\text{v}\) in order to remove the potential gradient in the barrier region. The unit was placed in an oil bath and maintained at a constant temperature of about 25°C for six days. At the end of the six days, there was no observable change in current passing through the sample at 0.7 \(\text{v}\) bias. The bias was removed for 2 hr. When the bias was restored, it was noted that the current had increased by about an order of magnitude. After an additional eight days in the biased condition, the current had not changed.

When the bias was removed, an electric field was established at the barrier which caused the interstitial atoms present in the barrier region to diffuse from the barrier toward the n-type side of the barrier. This removal of interstitial atoms from the p-type side to the n-type side of the barrier annealed out the type of damage which tends to make the p-type side less p type and transports it to the n-type side. Hence, both sides of the barrier are annealed back toward their initial condition, and the current increases back toward its initial value.

Transistor Irradiation

Attempts have been made to expose Philco surface-barrier transistors in the reactor. So far, attempts to measure the amplification characteristics of the surface-barrier transistor during irradiation have not been successful. However, measurement of the photo-emf developed across the collector and emitter barriers and a series of before and after measurements of the characteristic curves have been accomplished.

\textsuperscript{32}Howard Steele, private communication.
Since a sharp barrier is desirable for an emitter and a diffuse barrier is desirable for a collector, it would be expected that there might be some difference in the behavior of these barriers in a radiation field. The photo-emf's developed across such barriers during irradiation in hole 51N of the ORNL Graphite Reactor are shown in Fig. 8 as a function of the integrated neutron exposure. There is a considerable difference in the photo-emf's observed, but after $\sim 10^{14} \text{nvt}$ the barriers seem to become comparable.

Fig. 8. Photo-emf of a Philco Type L5106 Surface-Barrier Transistor as a Function of Integrated Neutron Flux.

The change in collector characteristic, with the emitter circuit open, taken after successive irradiations in hole 51N of the ORNL Graphite Reactor is shown in Fig. 9. As reported previously, this behavior compares with the characteristic of a diode biased in the reverse direction. After the third exposure, the sample was allowed to anneal for 18 hr at room temperature. The collector characteristic taken after the 18-hr anneal shows that the saturation current has dropped back toward its original value and that the leakage current, as indicated by the slope of the curve, has increased. The return of the saturation current toward its initial value agrees with the observation reported above, namely, annealing in the barrier due to the electrostatic field. Since the base material is $n$ type with a $p$-type surface, a similar barrier exists between the surface and the body of the crystal. Such annealing in this region would increase the conductivity of the surface and, hence, increase the leakage current. Increase in surface leakage is seen as an increase in the slope of the collector characteristic.

Fig. 9. Change in $I_{co}$ Characteristic of a Philco Type L5106 Surface-Barrier Transistor as a Result of a Series of 2-min Exposures at a Flux of $8.3 \times 10^{11} \text{nvt}$.

The change in the characteristic family of curves for grounded-base transistors after $9.96 \times 10^{12} \text{nvt}$ is shown in Fig. 10. Instead of an increase in $I_{co}$ there is a decrease in $I_{co}$ and there is no detectable change in slope. The separation of curves for different emitter currents is about the same as it was before bombardment. A circuit designed with normal engineering tolerances would still be operating, providing there had been no violent fluctuations of behavior in the interim. That the transition was smooth is well illustrated by Fig. 11, which shows $I_{co}$ at 1 v bias with different emitter currents as a function of $\text{nvt}$. With emitter current present, the collector current depends almost entirely on emitter current. The emitter characteristics, which compare to the forward characteristics of a diode, are much less sensitive to irradiation than the $I_{co}$ curve. For voltage biases greater than the barrier voltage, the forward current of a diode has been found to vary
in the same way as the bulk conductivity. Consequently, $I_c$ would be expected to change slowly for a transistor made of high-conductivity material.

The data for the Philco surface-barrier transistor were obtained from measurements made before and after irradiation. The curves show the stable accumulated change without the effects of annealing, photo-emf, and photoconductivity. Hence, the behavior of the unit in the presence of a radiation field is more complicated than these data show.

Irradiation of a Silicon Junction Diode

In previous irradiations of silicon diodes, annealing of the specimens occurred as a result of reactor shutdowns; and the influence of these annealing effects was, as a consequence, reflected in the data obtained. Thus, in order to eliminate this undesirable feature, a new experiment was performed such that irradiation was continuous and equilibrium conditions were maintained during the entire course of the exposure. The diode was irradiated in hole 51N of the ORNL Graphite Reactor (Fig. 12), and the irregularities which

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34 J. C. Pigg and C. C. Robinson, ORNL-1762, p 78 (Secret).

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Fig. 10. Change in Collector Characteristic of a Philco Type L5106 Surface-Barrier Transistor as a Result of an Irradiation of $9.96 \times 10^{12}$ $nvt$.

Fig. 11. Changes in Collector Currents of a Philco L5106 Surface-Barrier Transistor as a Function of Irradiation.

Fig. 12. Change in Forward and Reverse Currents (at 1 volt Bias) of a Silicon Junction Diode, National Semiconductor Products 1N138A-1, as a Function of Integrated Neutron Exposure.
appeared in the previous exposure did not occur. The forward and reverse currents at 1 v bias approach each other smoothly until the barrier is destroyed. After the destruction of the barrier, the conductance falls monotonically in the same manner as is observed in the bulk material for both n- and p-type samples.\textsuperscript{35}

\section*{THE EFFECT OF BOMBARDMENT ON OPTICAL ABSORPTION}

C. Edwards\textsuperscript{36} J. H. Crawford, Jr. C. M. Nelson

Alteration of the energy-level scheme of semiconductors is generally accompanied by a change in their optical-absorption spectra. Consequently, since it is well known that bombardment by fast particles has a pronounced influence on the distribution of energy levels in germanium and silicon, an effect on the optical absorption of these materials would be expected as well. In the case of silicon, the effect has been observed and is quite pronounced;\textsuperscript{37,38} an absorption band at 1.75 \( \mu \), which increases in amplitude with fast-neutron exposure, appears in irradiated specimens, and considerable absorption extending from 1.0 \( \mu \) (the absorption edge) to 1.50 \( \mu \) is developed. The discrete band at 1.75 \( \mu \) is not accompanied by photoconductivity, and it sharpened with decreasing temperature in the manner expected for electronic transitions between discrete states. Consequently, absorption in this wavelength range is presumed to result in excitation of an electron in a localized defect state in the forbidden band to its localized excited state. The continuous absorption near the band edge, on the other hand, is accompanied by photoconductivity at low temperatures, leading to the conclusion that absorption in this wavelength range (1.0 to 1.50 \( \mu \)) excites electrons to the conduction band, or excites holes to the valence band, or both.

The optical absorption of irradiated germanium has also been investigated,\textsuperscript{39} but not nearly so extensively as for silicon. The results are not conclusive. Studies carried out by Burstein et al., in cooperation with members of the Solid State Division, indicated only a small additional absorption which was independent of wavelength and extended from the fundamental absorption edge to longer wavelengths.

Reported here are the results of preliminary experiments on the optical behavior of germanium, which have been carried out preparatory to a more detailed study of the effect of fast-particle bombardment. Particular emphasis has been given to the behavior of the fundamental absorption edge.

Several thin single-crystal specimens of germanium were measured before and after exposure on the Cary model 14 spectrophotometer. The wavelength range studied was from 1.58 \( \mu \) to 2.55 \( \mu \); the lower limit was set by the rapidly increasing fundamental absorption of germanium, and the upper limit was set by the range of the instrument. One germanium plate of 40 ohm-cm resistivity was ground and polished to a thickness of 8 \( \times \) 10\(^{-3}\) cm, and its absorption spectrum before and after a series of exposures at room temperature in the ORNL Graphite Reactor was measured at room temperature. The spectrum before exposure is shown in Fig. 13 in which absorbency (\( \log \frac{l_0}{l} \)) is plotted against wavelength. The apparent absorption at the longer wavelengths is due almost entirely to multiple reflections within the specimen, and the oscillatory behavior of the curve is produced by multiple interference. Since the reflectance of germanium is known (0.345) and since it is essentially independent of wavelength over the range of interest, the values of true absorbency can be obtained by means of the relations given by Barnes and Czerny\textsuperscript{40} for monochromatic radiation. For the present specimen, the absorption coefficient \( \alpha \) is so small that to obtain it accurately from a specimen of this thickness is difficult. However, estimates from a thicker specimen with nearly the same carrier concentration indicate that the value is \( \alpha \approx 0.10 \).

The effect of fast-neutron bombardment is shown in Fig. 14, where the increase in absorbency \( \Delta \alpha \)

\textsuperscript{35}J. W. Cleland \textit{et al.}, ORNL-1128 p 12 (July 31, 1951) (Secret).

\textsuperscript{36}Summer employee of University of Tennessee.


Fig. 13. Optical-Absorption Spectrum of High-Purity Germanium.
Fig. 14. Change in Optical Absorption of Germanium as a Result of Fast-Neutron Bombardment Plotted as a Function of Wavelength.

is plotted against wavelength $\lambda$ after successive irradiations: curve 1, after $1.2 \times 10^{17} \text{nvt}_f$; curve 2, after $2.4 \times 10^{17} \text{nvt}_f$; and curve 3, after $4.2 \times 10^{17} \text{nvt}_f$. The results at short wavelengths were found to be poorly reproducible, and investigation revealed that this resulted from heating of the specimen by the light source (for the arrangement used in these curves, the light was sent through the monochromator after it passed through the specimen). Any nonreproducible heating would cause a scatter in the results, since the energy gap of germanium is temperature dependent to the extent of $-4 \times 10^{-4}$ ev/°C. Such an effect would of course be greater when the slope of the $\alpha$ vs $\lambda$ curve, at the wavelength in question, is greater; and, hence, it is evident only in the sharply rising fundamental absorption region. By use of the alternative optical path, that is, sending the light through the monochromator before it strikes the sample, this spurious effect is removed, since in this case the radiant energy incident on the specimen is negligible. Curve 4 was obtained in this manner by comparing the spectrum of the specimen after a dosage of $6 \times 10^{17}$ neutrons/cm$^2$ with that of the original after a suitable temperature correction. It is thus apparent that the true difference in absorption at short wavelengths is somewhat less than that indicated by curves 1, 2, and 3.

The form of the curves of Fig. 14 reveals that, for wavelengths beyond the fundamental absorption region, an essentially constant increase in $\alpha$ results from neutron bombardment. The increase in $\alpha$ with exposure at 2.00 $\mu$ is shown in Fig. 15. An

Fig. 15. Absorption Coefficient of Germanium at 2.00 $\mu$ Plotted as a Function of Fast-Neutron Exposure.
initial linear increase from a very small value, which saturates after about $5 \times 10^{17}$ neutrons/cm$^2$, is indicated. Near the absorption edge, however, $\alpha$ increases more rapidly as the wavelength gets shorter. These preliminary results lead then to the tentative conclusion that the slope of the $\alpha$ vs $\lambda$ curve in the range of fundamental absorption increases markedly with exposure. This behavior is evidently more complex than a simple shift of the absorption edge toward longer wavelengths.

A preliminary annealing study was also performed. The specimen receiving $6 \times 10^{17}$ neutrons/cm$^2$ was given two 151°C anneals for 20 min each. The results are shown in Fig. 16, where the increase in absorbency over that for unirradiated material is plotted against $\lambda$. As is evident from these curves, almost all the recovery of $\Delta \alpha$ occurs after the first anneal. It is interesting to note that the recovery is not uniform over the range of $\lambda$ covered; the change of $\Delta \alpha$ at 1.58 $\mu$ is approximately three times greater than that at 1.9 $\mu$. On a relative basis, however, the recovery is more nearly uniform.

![Graph showing the effect of annealing on the increase in optical absorption of germanium.](image)

**Fig. 16.** Effect of Annealing on the Increase in Optical Absorption of Germanium.

It is too early to attempt to draw any definite conclusions from these preliminary results. However, the sharpening of the rise of absorption in the fundamental region is quite interesting and gives an indication as to the direction future work should take. The mechanism of absorption near the fundamental band edge of germanium has been worked out theoretically by Bardeen and co-workers\footnote{L. H. Hull, J. Bardeen, and F. J. Blatt, *Phys. Rev.* 95, 559 (1954).} and has been confirmed experimentally by Dash and Newman\footnote{W. C. Dash and R. Newman, *Phys. Rev.* 99, 1151 (1955).}. Because of the complexity of the band structure, the absorption that sets in near 1.6 $\mu$ is not due to a direct optical transition from the valence band to the conduction band, but rather is one involving a phonon interaction. This results from the fact that the minimum energy of the conduction band and the maximum energy of the valence band do not fall at the same position in momentum space or $K$ space. The conduction band has minima which fall near the Brillouin zone in the [111] directions of $K$ space, while the valence bands have maxima at the center of the zone or at $K = 0$. Hence, the phonon energy for the direct or $K$-conserving transitions is greater than the thermal-energy gap. The selection rules for optical transitions are relaxed to some extent by lattice vibrations, and this occurs to a sufficient extent that the observed fundamental absorption edge corresponds to that expected from the thermal-energy gap. However, since the probability of such thermal perturbations depends on the density of phonons, the indirect transitions are temperature dependent.

Consequently, in the investigation of the effect of perturbations, resulting from radiation-induced lattice disorder, on the transition probabilities, the perturbing effect of lattice vibrations can be suppressed by lowering the temperature. Another matter which should be investigated more thoroughly is the effect of radiation on the direct transitions which occur at shorter wavelengths. Therefore, as future work, the effect of exposure on the fundamental absorption region should be studied on thinner specimens and, also, studied as a function of temperature. A search for a structure, such as that observed in silicon, which is due to transitions between localized defect states, at longer wavelengths ($>2.6 \mu$) is also planned.

**THE OPTICAL-ABSORPTION BEHAVIOR OF IRRADIATED SOLIDS**

C. M. Nelson

During this period, research has continued on fused silica\footnote{C. M. Nelson, *Solid State Seminans. Prog. Rep. Aug. 30, 1955, ORNL-1943, p 32.}. The studies have been extended to include crystalline quartz (both natural and

synthetic), synthetic sapphire, and synthetic rutile. A comprehensive set of irradiations has just been completed in which the relative flux, in the range $1 \times 10^{17}$ to $3 \times 10^{29} \text{nvt}^{-1}$, and the irradiation temperatures were approximately the same for all the specimens.

These irradiations have been carried out in a special facility in the LITR. Since all the materials to be irradiated are unaffected by water, it was very convenient to insert them directly into the cooling water of the reactor. Thus, the samples are kept below 105°F, or 41°C. The arrangement is very simple; it consists of an aluminum tube, one end of which projects into the fuel-element assembly and the other end extends out of the top cover plate. The bottom portion near the fuel elements has many holes drilled in it for easy flow of the cooling water. Also, there are a number of holes at intervals up the tube. Since the top is open, the sample containers can be dropped, at any time the reactor is operating, directly into the water filling the tube. For short exposures, an aluminum wire is attached to the container so that it can be retrieved easily. For long exposures, the containers were freely dropped. At the end of August the whole tube was removed. After cooling for several weeks, the containers were dumped out. The samples will be examined as soon as the containers are cool enough to handle. Diamond-dust specimens were included in these irradiations in order to provide a measure of the total dose of fast neutrons.

The Cary model 14 spectrophotometer was received the last of April and has been extensively used. Initial troubles were annoying but were gradually overcome. By sweeping the instrument with dry nitrogen, it is possible to measure optical absorption from 1850 to 26,000 Å. The extended ultraviolet range has already proved useful in proving the existence of an absorption band in quartz and fused silica below 2000 Å, as noted below.

Unfortunately, the complete set of absorption data could not be completed for this report, but the qualitative features of the data can be described. Synthetic quartz, obtained from General Electric Ltd. of England, shows an immediate increase in optical absorption below 2000 Å with $10^{17} \text{nvt}^{-1}$, but there is no indication of the 2120 Å band until $10^{18} \text{nvt}^{-1}$. At $10^{19} \text{nvt}^{-1}$, this band is very prominent and has a sharp peak. Also at $10^{19} \text{nvt}^{-1}$, the absorption value at 1850 Å, which is always highest at the lower irradiations, becomes about the same as the 2120 Å band peak. The profile of the long-wavelength side of the 2120 Å absorption band indicates that the 2600 Å absorption band observed in optically bleached fused silica is present in crystalline quartz, too. In quartz the unresolved absorption band near 2120 Å is approximately at the same position as in the vitreous silica. It will be interesting to see if both bands are at the same positions that were observed in Corning high-purity silica after optical bleaching. The brown coloration decreased in intensity after $10^{19} \text{nvt}^{-1}$.

Plates for use in these experiments were cut from a bar of high-purity natural quartz. This material behaved a little differently from the synthetic quartz in that the absorption below the 2000 Å band is about the same as in the vitreous silica. The brown color is not as intense as in synthetic quartz.

Included in the vitreous-silica specimens were samples of Corning high-purity No. 7940 silica, General Electric type III special high-purity vitreous silica, and Amerasil optical-grade clear fused quartz. Each material showed different degrees of coloration both in the visible and the ultraviolet regions. Whereas the Corning material did not color in the visible region at all, the G-E and Amerasil materials turned purple, though the Amerasil was not as densely colored as the G-E specimens. By the time the bombardment reached $10^{19} \text{nvt}^{-1}$, most of the visible coloration was gone. With reference to the 2120 Å band, the differences between the materials was remarkable. When bombarded with $10^{17} \text{nvt}^{-1}$, the Amerasil specimen gave about ten times as much absorption as the Corning specimen and about two times as much as the G-E specimen. The differences were gradually lessened, but even at $10^{19} \text{nvt}^{-1}$ the Amerasil material gave about 1.5 times the optical absorption as the Corning material, with the G-E material close to Amerasil in absorption.

These large differences in optical absorption at 2120 Å are a little disillusioning, however, since they do not take into account the effect of the increased absorption below 2000 Å. The observed absorption at 2120 Å lies on the side of this absorption below 2000 Å and thus cannot be easily resolved from it. There is definitely either an absorption band below 1850 Å or an increase in
absorption on the edge of the fundamental absorption band. Except for short exposures, all silica specimens, whether vitreous or crystalline quartz, show a minimum in absorption around 2000 Å. As noted above, an increase in absorption in this region for bombarded synthetic quartz is the only ultraviolet absorption until about $10^{18} \text{nvt}$/, after which the 2120 Å band can be noticed. It was observed that in a Co$^{60}$ gamma-irradiated Corning silica specimen this far-ultraviolet absorption is not so prominent as in these fast-neutron-irradiated samples.

As discussed in the previous report, it was proposed that the ultraviolet absorption bands were due to the formation of free radicals. A study has been made of the difference in rate of coloration by Co$^{60}$ gamma radiation with temperature and different materials. The results discussed above in the present report on fast-neutron irradiations can also be fitted into this scheme of free-radical formation. In fact, on comparison of the behavior of natural and synthetic quartz, it appears that the concept of trapped electrons or holes at vacancies would have to be discarded. The rate of ultraviolet coloration of synthetic quartz is very much greater than that for natural quartz and both are less than that for the vitreous silica.

If coloration is due to electrons or holes trapped at definite lattice configurations, the crystalline material would be expected to offer the best opportunities for vacancy configurations. Since the vitreous materials colored at a faster rate, the color centers do not appear to be due to trapped electrons or holes at lattice sites.

It has been shown$^{45}$ that fast-neutron irradiation of quartz produces a silica glass and, in fact, induces permanent damage at $\sim 2 \times 10^{19} \text{nvt}$/, The natural-quartz specimen did not show much absorption even with $10^{18} \text{nvt}$/, However, at $10^{19} \text{nvt}$/, all materials showed a very rapid rise in optical absorption and the formation of a band at 2120 Å, indicating that order was not necessary for color formation. With the start of disorder in the quartz lattice, radicals would be expected to form more easily.

In the previous semiannual report$^{44}$ Co$^{60}$ gamma irradiation of Corning silica was mentioned as producing less indication of the 2570 Å band than did fast-neutron irradiation. Subsequent measurements on gamma-irradiated samples which were bleached with a mercury-vapor lamp, in the same manner as previously, proved that this less prominent band is also present. This is in contrast to the results obtained by Cohen,$^{46}$ who stated that this band was not observed in his samples.

Thus, it appears that fast neutrons or ionizing radiation produces three types of coloration in crystalline quartz or vitreous silica. Two absorption bands have been identified at 2570 and 2120 Å and the increase in absorption noted near the limit of the range of the instrument may be due to another absorption band or to a general increase in the fundamental absorption.


ENGINEERING PROPERTIES

O. Sisman

INFRARED SPECTRA OF PLASTICS AND ELASTOMERS AFTER IRRADIATION

W. C. Sears     W. W. Parkinson
W. K. Kirkland

In the previous report,\textsuperscript{1} the investigation of the changes in molecular structure of irradiated polymers by infrared analysis was described. Infrared absorption spectra of thin films of various organic polymers were measured before and after irradiation with Co\textsuperscript{60} gamma rays and nuclear-reactor radiation. The doses and conditions of irradiation were presented, and the techniques of the spectral measurement were discussed. Changes were noted in the absorption bands characteristic of certain structural groups in polystyrene, polyethylene, polybutadiene, crude and extracted natural rubber, GR-S rubber, and polyvinyl chloride. Other polymers were irradiated, but satisfactory infrared records of radiation effects were not obtained.

In the earlier report, it was observed that most of the polymers oxidized extensively upon being exposed to air after having been irradiated sufficiently to produce perceptible changes in the infrared spectrum. Infrared measurements have been continued on the same polymer specimens exposed to air. Polystyrene, which had received the largest dose of all the materials, showed the highest rate of oxidation. Polystyrene specimens irradiated in a vacuum were measured after periods of about 100 days' exposure to air, and oxidation was shown to be still in progress. The O–H bond (3450 cm\textsuperscript{-1}) and the C=O bond (1700 cm\textsuperscript{-1}) were still increasing considerably after such periods.

Three polystyrene specimens were irradiated together in vacuum. Then, one was stored in air, one in oxygen, and one in helium saturated with water vapor and contaminated with perhaps 1 or 2% oxygen. The specimen stored in oxygen oxidized slightly faster than the one stored in air, while the specimen exposed to the mixture of helium and water vapor required three times as long as the other two to show a given increase in the O–H or C=O bands. This indicates that it is the oxygen which reacts, rather than the water vapor. Quantitative rates of reaction cannot be calculated until precise infrared absorption coefficients are established.

Additional spectral curves on irradiated polybutadiene show that it oxidizes at a rate comparable to the other polymers. After periods of as long as 250 days, the O–H and C=O bands were still growing (Fig. 17). Measurements of irradiated GR-S rubber stored for 250 days in air show that it is also continuously oxidized (Fig. 18). Both crude and extracted hevea (natural rubber) showed little postirradiation oxidation of the polymer itself upon initial exposure to air, probably because the oxygen was consumed by the antioxidant (phenyl-β-naphthylamine, present to the extent of about 1%); however, on extended exposure to air, the specimens showed about as much oxidation as the other materials.

Since natural rubber and some synthetic rubbers oxidize under normal conditions of storage, a specimen of extracted hevea prepared at the same time as the irradiated specimens and stored for a year in air was measured. It showed about one fifth the concentration of oxidation products as that contained by a similar specimen irradiated to a dosage of 2.2 \times 10\textsuperscript{9} rads and exposed to air for 69 days.

Recent spectra of polyvinyl chloride showed a moderate tendency to form oxidation products containing the C=O group, as indicated by the growth of a very broad peak having a maximum at 1725 cm\textsuperscript{-1}. The O–H band in the 3400 cm\textsuperscript{-1} region developed very slowly, as shown by Fig. 19, and did not become appreciable until the measurement that was made after 275 days' exposure to air. This contrasts with the oxidation reaction of the other polymers, which show growth of C=O and O–H bands at similar rates.

In order to estimate the concentration of the molecular groups indicated by the infrared absorption peaks, it is necessary to determine the absorption coefficients of the groups in their peak absorption regions and in regions where they contribute to the absorption by other groups. It is also necessary to determine the thickness and density of the specimens. The absorption coefficients are being determined on CS\textsubscript{2} solutions of various alkane standards and octene isomers.

Fig. 17. Infrared Spectra of Polybutadiene Irradiated in Vacuum.
Fig. 18. Infrared Spectra of Irradiated GR-S Rubber.
Fig. 19. Infrared Spectra of Polyvinyl Chloride Irradiated in Vacuum.
Since it is known that the density changes during irradiation, the densities published for the unirradiated polymers cannot be used. The densities of the polystyrene, natural rubber, and polyvinyl chloride specimens have been determined by the flotation method in aqueous salt solutions of graded densities. In order to determine the thickness of the specimens, methods must be selected that are appropriate to each material because of the nonuniformity, asymmetry, and softness of some of the specimens. The thickness of all the specimens can be determined to varying degrees of precision from the density and the weight of a section of measured area. For polystyrene, the value obtained by this method, the one obtained by direct measurement with a calibrated microscope, and that determined from interference peaks in the infrared spectrum agreed to ±5%. Polyvinyl chloride was not sufficiently uniform to give interference peaks; but the agreement was also about ±5% for the thickness values obtained from the density method, from the average of comparator readings, and from microscopic measurements.

As a continuation of the program of irradiating specimens for infrared analysis, six specimens, three of polyethylene terephthalate and three of poly-2-methylstyrene, have been irradiated for a week in position C-46 of the LITR. The irradiation exposures ranged from about 5 x 10^14 to 5 x 10^16 rods. The specimens were irradiated as unmounted films, since earlier samples mounted on wire frames were subject to splitting before an adequate dosage could be reached. The results of these irradiations are not yet available.

EFFECTS OF HIGH-ENERGY RADIATION ON POLYMERS

W. W. Parkinson  W. K. Kirkland
Solid State Division
R. F. Hombach
Glenn L. Martin Company

Since important changes, from both a technical and a fundamental standpoint, take place during irradiation of polymeric materials, investigations along both these lines are being carried out. Cross-linking and scission of the polymeric chains can be studied by following the changes in molecular weight and by the formation of insoluble gel.

As examples of vinyl polymers that differ greatly in radiation resistance, polystyrene and polymethyl methacrylate have been selected as experimental materials. The viscosities of solutions of varying concentrations of commercial polystyrene in toluene have been measured in order to determine its molecular weight. Also, samples of various average molecular weights have been prepared from commercial polystyrene by a fractional precipitation technique. Methanol (as a nonsolvent) was added to a benzene solution of polystyrene until turbidity was noted in the mixture. The mixture was warmed to disperse the cloudiness and was then cooled to fractionally precipitate, from the more uniform mixture, a portion of the polymer consisting of the higher-molecular-weight material. The supernatant liquid was poured off and treated with additional methanol in order to throw down the next-lower-molecular-weight fraction. The precipitated polymer fraction was in some cases fractionated again from benzene, but in all cases it was finally dissolved and reprecipitated from methyl ethyl ketone so as to get the precipitate in a form more easily filtered and dried. In this manner the stock polystyrene was separated into six molecular-weight fractions.

Viscosity measurements were made on solutions of each of the six fractions. The viscosities indicated that the molecular weights of the six fractions ranged from 20,000 to 500,000.

A similar fractionating method was employed to separate polymethyl methacrylate into five molecular-weight fractions. For these separations, acetone was used as the solvent and methanol as the precipitant. The final precipitation of each polymer fraction dissolved in acetone was carried out by pouring the solution into hexane. The molecular-weight determinations on these fractions have not been completed.

As a continuation of the earlier study of the effects of radiation on the engineering properties of polymers, some new materials are being irradiated and tested. Samples of fluorobutyl rubber...
acrylate, which has shown promise as a solvent-resistant gasket and sealant material, have been irradiated in water-cooled hole 19 of the ORNL Graphite Reactor. This material differs from the previously tested halogenated materials in that it has halogen atoms attached to carbon atoms in the side chains rather than to atoms in the main polymer chain. The samples in the form of sheets were prepared, according to the usual methods of rubber compounding, from the ingredients (in parts by weight) shown below.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Philblock A</td>
<td>35</td>
</tr>
<tr>
<td>Paraffin</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1</td>
</tr>
<tr>
<td>Triethylene tetramine</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The material was cured at 320°F for 30 min.

The specimens were tested according to the method described previously, and the properties before and after irradiation are listed in Table 3. The tabulated values are average values for several specimens. The irradiation of additional specimens to larger dosages is in progress.

RADIATION STABILITY OF CERAMIC MATERIALS
C. D. Bopp R. L. Towns

Radiation-Induced Density Changes

The changes induced by radiation in some of the physical properties of certain ceramic materials have been reported. In order to further evaluate the effects of radiation, the density changes in this same group of materials have been determined. The density changes are given in Table 4. The weight or thickness changes for the C exposure were considerably more scattered than these data; the materials were immersed in water during the C exposure and lost weight both from chipping and from the solvent action of the water. For the A and B exposures the weight and thickness changes were not measured, since the materials were coated with corrosion products, and the coatings were removed in order to make the density measurements. The density measurements are less sensitive for the porous materials than for the nonporous materials. Within the sensitivity indicated in Table 4, sintered Al₂O₃, pressed BeO, pressed ZrO₂, and pressed TiO₂ were unchanged. For many of the materials which did change, the change is nearly saturated; that is, it is nearly the same for all three exposures. The integrated epithermal flux was greater, but the integrated thermal and gamma fluxes were less, for the B exposure than for the C exposure because of the differences in flux distribution for the different reactors. For spinel, porcelain, and zircon the change in density is greatest for the B exposure, in accord with a fast-neutron effect; but for mica and sapphire a large part of the change for the C exposure must result from thermal-neutron or gamma radiation. The increase in density of silica glass, pyrex glass, and plate glass contrasts with the decrease of the other materials and may be ascribed to closer packing. In the case of the silica glass and pyrex glass it appears that for the B exposure a second process cancels out part of the change observed for the shorter, A, exposure.


<table>
<thead>
<tr>
<th>Specimen</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose, nvt</td>
<td>0</td>
<td>0.45 x 10¹⁸</td>
</tr>
<tr>
<td>Dose, rads</td>
<td>0</td>
<td>0.18 x 10⁹</td>
</tr>
<tr>
<td>Tensile strength, psi</td>
<td>1070</td>
<td>658</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>127</td>
<td>22</td>
</tr>
<tr>
<td>Durometer hardness</td>
<td>70</td>
<td>86</td>
</tr>
<tr>
<td>Weight change, %</td>
<td>-7.3</td>
<td></td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>1.6210</td>
<td>1.6257</td>
</tr>
<tr>
<td>Electrical resistance, ohm-cm</td>
<td>4 x 10¹⁰</td>
<td>3 x 10⁵</td>
</tr>
<tr>
<td>Dielectric strength, v/mil</td>
<td>130</td>
<td>119</td>
</tr>
</tbody>
</table>

TABLE 4. THE EFFECT OF REACTOR RADIATION ON THE DENSITY OF CERAMICS

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Reactor</th>
<th>Integrated Epithermal Flux ($\times 10^{19}$ nvt)</th>
<th>Integrated Thermal Flux ($\times 10^{19}$ nvt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Graphite</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>Graphite</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>MTR</td>
<td>3–6</td>
<td>30–60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Preirradiation Density (g/cm$^3$)</th>
<th>Change After Irradiation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_2O_3$, sapphire</td>
<td>$3.984 \pm 0.001$</td>
<td>$-0.33$</td>
</tr>
<tr>
<td>$Al_2O_3$, sintered</td>
<td>$3.559 \pm 0.001$</td>
<td>$1$</td>
</tr>
<tr>
<td>BeO</td>
<td>$2.84 \pm 0.03$</td>
<td>$0.3$</td>
</tr>
<tr>
<td>ZrO$_2$ 71</td>
<td>$5.63 \pm 0.02$</td>
<td>$0.4$</td>
</tr>
<tr>
<td>TiO$_2$ 192</td>
<td>$4.01 \pm 0.01$</td>
<td>$0.3$</td>
</tr>
<tr>
<td>Zircon 475</td>
<td>$3.73 \pm 0.01$</td>
<td>$-8$</td>
</tr>
<tr>
<td>Mica</td>
<td>$2.845 \pm 0.001$</td>
<td>$-2.4$</td>
</tr>
<tr>
<td>Brazilian quartz</td>
<td>$2.65 \pm 0.01$</td>
<td>$-14.3$</td>
</tr>
<tr>
<td>Spinel</td>
<td>$3.61 \pm 0.01$</td>
<td>$-0.4$</td>
</tr>
<tr>
<td>Steatite 228</td>
<td>$2.796 \pm 0.005$</td>
<td>$0.3$</td>
</tr>
<tr>
<td>Forsterite 243</td>
<td>$3.056 \pm 0.004$</td>
<td>$-0.9$</td>
</tr>
<tr>
<td>Porcelain 576</td>
<td>$3.414 \pm 0.006$</td>
<td>$-0.5$</td>
</tr>
<tr>
<td>Silica glass</td>
<td>$2.203 \pm 0.005$</td>
<td>$+2.1$</td>
</tr>
<tr>
<td>Pyrex glass</td>
<td>$2.217 \pm 0.003$</td>
<td>$+2.4$</td>
</tr>
<tr>
<td>Plate glass</td>
<td>$2.509 \pm 0.001$</td>
<td>$+0.44$</td>
</tr>
<tr>
<td>Lead glass</td>
<td>$4.951 \pm 0.003$</td>
<td>$-1.5$</td>
</tr>
</tbody>
</table>

A disk-shaped specimen, $\frac{3}{4}$ in. in diameter by 20 mils in thickness, was weighed in kerosene on a semimicro balance; because of the high temperature coefficient of the density of kerosene, a correction was made for variations in room temperature. In order to minimize the effect of surface tension, the specimen was suspended so that the surface of the kerosene was intercepted by a single strand of orlon of about 1 mil diameter. In order to obtain uniform penetration of kerosene into porous materials, the air was removed in a vacuum dessicator while the specimen was under kerosene.

It is believed that the apparent increase in density for cordierite may be the result of a radiation-induced change in pore size and, therefore, in the amount of penetration by the kerosene, since the result was found to depend on the time in the dessicator. Insensitivity to the time in the dessicator is taken as evidence of absence of an effect of pore size for the materials listed in Table 4. Since different specimens were used for preirradiation and postirradiation measurements, the sensitivity was limited by nonhomogeneity of the materials.
Temperature Dependence of the Elastic Constants and the Internal Friction

The apparatus for measuring vibration characteristics is being modified so as to permit measurements from -100 to +500°C. The heat shield (Fig. 20) is insulated from the surroundings by a tank which is filled with radiation shielding and evacuted; the heat shield can be cooled with liquid nitrogen or heated electrically. In order to minimize the effect of temperature on the position of the driver on the specimen (since this affects the mode of vibration), the driving mechanism is made in two parts: the exciter and the cap. The cap, which contacts the specimen, is mounted coaxially with respect to the specimen support. The magnetostrictive exciter, which consists of a nickel tube wrapped with a copper coil, is welded to the side of the tank. Ball bearings permit both the cap and the specimen support to move in arcs perpendicular to the specimen; contact between these mobile pieces is maintained as a result of their respective weights. The large mass of the cap makes it insensitive to resonances from either the exciter or the ball bearings and, therefore, serves to isolate the specimen from interfering resonances. Because of the high rigidity of the cap, resonances from it do not contribute any appreciable interference, since these resonances are of relatively high frequency and low amplitude. The capacitance-type vibration pickup consists of a metal block, mounted near the specimen, with a Lavite insulator. Plotting of the resonance curves has been made automatic by varying the frequency of the oscillator with a synchronous motor drive and feeding the vibration pickup signal to a recorder. The time required to reach thermal equilibrium may be reduced by strapping both the specimen support and the cap to the heat shield with flexible copper braid. Time may also be saved by providing duplicate driving caps, specimen supports, and vibration pickups in order that two specimens may be run simultaneously.

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Fig. 20. Vibration Testing Apparatus.
Stored Energy in Irradiated Ceramics

A calorimeter is being built to measure stored energy in small samples. The calorimeter is a modification of an adiabatic type in that, although heat exchange with the surroundings is reduced by a heat shield, a correction is made for the small temperature differences which are allowed between the calorimeter and the shield. This modification greatly simplifies control, and it is applicable to the case where the release in stored energy is in excess of the specific heat so that the temperature of the sample is raised above the temperature of the shield. The heat shield (Fig. 21) is made in two parts in order to facilitate mounting the thermocouples and the crucible. The outer shield serves as a vacuum-tight housing and in addition provides a uniform temperature field; it consists of a copper pipe enclosed inside and outside by concentric steel pipes. Copper is used because of its high thermal conductivity; steel is used for strength at high temperatures (800–1000°C). This design supersedes the one involving a single brass block, which was found unsuitable, since zinc vapor was evolved by the brass in vacuum at high temperature. One end of the shield is heated in a Globar furnace. The crucible is maintained at approximately the temperature of the inner shield by passing a direct current through it. In order to determine the electric power a separate set of leads is used to measure the voltage drop across

![Fig. 21. Calorimeter.](image-url)
the crucible. The emf of the differential thermocouple is measured by a galvanometer, and the sensitivity is about 0.001°C. Stray emf's, as a result of inhomogeneity in the differential-thermocouple lead wires (which must pass through a large temperature gradient), are canceled by zeroing the galvanometer with a shorting switch located inside the high-temperature zone.$^{11}$ It is expected that time may be saved by running two samples simultaneously in duplicate crucibles, each sample being measured with its own set of differential thermocouples and current leads.

RADIATION METALLURGY

J. C. Wilson

HRP RADIATION METALLURGY
R. G. Berggren        J. C. Wilson

Irradiation at temperatures less than 200°F of impact and tensile specimens of a variety of steels has been completed in the HB-3 facility of the MTR, and testing is in progress. Some of the impact testing has been completed, and the results are presented below.

8½% Nickel Steel

Subsize Izod specimens of this steel irradiated to approximately $10^{20}$ neutrons (1 mev) showed an increase in fracture transition temperature and a decrease in fracture energy similar to the results previously reported. Fracture energy values for both irradiated and unirradiated specimens in this latest series of tests were about 50% higher than corresponding values in the previously reported tests on the same alloy. This discrepancy is probably due to differences in specimen preparation rather than to changes in the testing machine. Tests made concurrently on other alloys did not show this discrepancy. At $1 \times 10^{20}$ neutrons, the yield stress increased from 92,000 to 183,000 psi, and the tensile strength increased from 119,000 to 184,000 psi. Elongation in eight diameters decreases from 30 to 5.5%. At $10^{20}$ neutrons, there was still about 2% uniform elongation (occurring at about constant nominal stress) before necking began.

Carilloy T-1

This alloy is a quenched and tempered low-alloy steel possessing good low-temperature ductility. Results of notched-bar impact tests on this steel after irradiation in the LITR and MTR are presented in Fig. 22. The effects of irradiation in raising the temperature for transition from brittle to ductile fracture of the subsize Izod specimens and in decreasing the energy absorbed in “ductile” fracture are clearly shown.

---

Fig. 22. Effect of Radiation on Impact Energy of Quenched and Tempered Carilloy T-1 Steel.
Tensile data at $1.7 \times 10^{19}$ and $10 \times 10^{19} nvt_f$ showed (1) the yield stresses increased from 120,000 psi (unirradiated) to 170,000 and 186,000 psi, respectively, (2) the tensile strength went from 171,000 to 187,000 psi, and (3) the elongation in eight diameters decreased from 14 to about 4%. Prenecking elongation was of the order of 1% after irradiation, compared to 8% before irradiation.

ASTM A 212 Grade B Carbon-Silicon Steel

Tests were conducted on subsize Izod impact specimens of two different heats of ASTM A 212 grade B steel. Specimens of one steel were in the hot-rolled condition; and specimens of the second steel, made by ASTM A 300 fine-grain practice, were in the normalized condition. Chemical analyses of these steels will be available later. Figure 23 gives the results of impact tests on the steel that was in the hot-rolled condition, and Fig. 24 gives the results for the steel that was in the normalized condition. Both steels exhibited a marked increase in fracture transition temperature and a decrease in "ductile" fracture energy.

**Tensile Data**

The observations below are preliminary in the sense that some important quantities (such as, reduction of area) have not yet been measured, and all specimens in the test series have not been broken. Preliminary results from tensile tests of the carbon steels and the low-alloy steels that were used for the impact tests and that had been irradiated to neutron dosages of $10^{19}$ to $10^{20} nvt$ have shown several unusual features. In the more radiation-sensitive steels, high dosages reduce the work-hardening capabilities to low values. As a result, the yield stress and the ultimate stress are practically identical, and only about 1 to 2% uniform elongation precedes necking. The uniform elongation decreases with increasing dosage. All the steels tested showed extension during necking. The postnecking elongation

---

**Table 1**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>AMOUNT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARBON</td>
<td>0.20</td>
</tr>
<tr>
<td>MANGANESE</td>
<td>0.82</td>
</tr>
<tr>
<td>PHOSPHORUS</td>
<td>0.018</td>
</tr>
<tr>
<td>SULPHUR</td>
<td>0.030</td>
</tr>
<tr>
<td>SILICON</td>
<td>0.22</td>
</tr>
</tbody>
</table>

---

**Figure 23**

Effect of Radiation on Impact Energy of Hot-Rolled ASTM A 212 Grade B Carbon-Silicon Steel.
Fig. 24. Effect of Radiation on Impact Energy of Normalized ASTM A 212 Grade B Carbon-Silicon Steel.

appears to be dose sensitive but to a lesser degree than the prenecking elongation. Fine-grained steels appear more radiation resistant than coarse-grained steels, but a fine-grain size seems to be only a necessary, not a sufficient, condition for radiation resistance.

In high-purity iron the shape of the stress-strain curve is strongly affected by a factor-of-40 increase in strain rate. Specimens of coarse-grained (supercritical anneal) and fine-grained (subcritical anneal) iron irradiated to 3.6 x 10^{19} nvt were tested at strain rates of 0.05 and 2.0 in./min. At the slower strain rate both the fine-grained and coarse-grained materials showed reduced uniform (but not postnecking) elongation after irradiation, but the stress-strain curve of the fine-grained material was unusual in that the yield strength exceeded the conventional ultimate strength. At the higher strain rate neither material showed appreciable uniform elongation; virtually all elongation took place after the maximum load. Postnecking elongation, again, was not greatly affected.

Incomplete strain-rate studies on several fine-grained steels have indicated that high-strain-rate sensitivity is not a general characteristic of low-alloy irons or steels.

The data from all recent tests are being put on punched cards for easier handling of data. Upon completion of the present test series a complete report containing all data will be issued.

DUCTILITY MEASUREMENTS OF NICKEL AND SOME HIGH-NICKEL ALLOYS

T. C. Price  J. C. Wilson

Tensile tests were run on Inconel, nickel, and Nichrome V specimens in order to determine the temperature range at which a ductility minimum exists. The Nichrome V and Inconel specimens came from three different heats of metal: A, B, and C on the graphs. Two strain rates were used: 0.002 and 2.0 in./min. The gage-length portion of the specimens is 0.1500 ± 0.0010 in. in diameter and 0.60 ± 0.05 in. in length. Test temperatures ranged from 800 to 1600°F. Ductility measurements were taken in terms of per cent elongation and per cent reduction in area at fracture and at a longitudinal distance 0.50 in. from the fracture.

Nichrome V. — These specimens were annealed for 7 min at 1900°F in hydrogen. It can be seen from Figs. 25 and 26 that a ductility minimum exists between 1200 and 1400°F at the faster
strain rate but none exist at the slower rate. The scatter of results between different heats of metal at 1400°F at the faster strain rate should be noted.

**Fig. 25.** Effect of Temperature on Tensile Properties of Nichrome V, Heats A, B, and C, Tested at a Strain Rate of 2.0 in./min.

**Inconel.** The Inconel specimens were annealed 7 min at 1900°F in hydrogen. It is evident from Figs. 27 and 28 that, although the results of the different heats varied slightly, their general trend appears to be the same. At both strain rates the ductility is constant up to 1100°F, after which it increases rapidly with temperature. Some scatter can be noted between 1100 and 1250°F.

**Nickel.** The nickel specimens were annealed 7 min at 1600°F in hydrogen and came from only one heat. A definite ductility minimum can be seen at approximately 1400°F at the slower strain rate, but none is seen at the faster rate (Figs. 29 and 30).

The curves of ultimate strength vs temperature and yield stress vs temperature for all three metals were quite similar in shape; the yield stress remained fairly constant, and the ultimate strength gradually decreased with temperature.

**Fig. 26.** Effect of Temperature on Tensile Properties of Nichrome V, Heats A and C, Tested at a Strain Rate of 0.002 in./min.

**Fig. 27.** Effect of Temperature on Tensile Properties of Inconel, Heats A, B, and C, Tested at a Strain Rate of 2.0 in./min.
Fig. 28. Effect of Temperature on Tensile Properties of Inconel, Heats A, B, and C, Tested at a Strain Rate of 0.002 in./min.

At both strain rates, saw-tooth-shaped fluctuations appeared on the load recording chart of the tensile machine (Fig. 31) between the temperatures 400 and 1200°F for Nichrome V and 500 and 1200°F for Inconel. These fluctuations were accompanied by audible clicks and started immediately after the yield point, except at the lower temperature limit, where they began immediately before fracture. They terminated at a strain anywhere from a few hundredths of an inch to that at the fracture point. The fluctuations occurred greatest at 800°F and smallest at 400 to 500°F and at 1200°F; and their amplitude varied from 0 to 2260 psi stress, with occasional fluctuations up to 6000 psi near the fracture point.

Fig. 29. Effect of Temperature on Tensile Properties of Nickel Tested at a Strain Rate of 2.0 in./min.

Fig. 30. Effect of Temperature on Tensile Properties of Nickel Tested at a Strain Rate of 0.002 in./min.
Fig. 31. Stress-Strain Curve for Nichrome V Tested at 800°F at a Strain Rate of 0.002 in./min.
CHEMICAL EFFECTS OF NUCLEAR REACTIONS

THE REACTION OF BORIC ACID WITH SOME PYRIDINE BASES

M. T. Robinson

In a previous report, the reaction of orthoboric acid, $H_3BO_3$, with pyridine was described. The observations have been extended to include a number of pyridine derivatives, all of which reacted readily with $H_3BO_3$. The reaction products appear to be orthorhombic and have the lattice constants given in Table 5. Chemical analytical data (Table 6) do not lead to simple formulas for these materials. In general, the compounds correspond more or less to the metaborate composition ($B_2O_3$:$H_2O = 1$:$1$); the largest deviations occur in those cases where the solubility of water in the organic base is least. Incomplete removal of the water produced by conversion of $H_3BO_3$ to HBO$_2$ leaves products of variable composition. The compounds of boric acid with 2,3- and 2,6-lutidine, 2,4,6-collidine, and quinoline are substantially altered by washing with toluene. The x-ray diffraction patterns taken before and after this treatment are strikingly different, but the same sets of lattice constants suffice to explain all the observed reflections.

The most satisfactory rationalization of the x-ray data is to interpret all the compounds as being based ultimately on the layered structure of orthorhombic HBO$_2$(III), which has been reported to be constructed of parallel sheets of $B_2O_6^{--}$ ions bound together in the plane by hydrogen bonds.

---


---

<table>
<thead>
<tr>
<th>Base</th>
<th>$a_0$ (Å)</th>
<th>$b_0$ (Å)</th>
<th>$c_0$ (Å)</th>
<th>Experimental Density $^b$ (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>16.9</td>
<td>17.7 (±0.2)</td>
<td>14.6</td>
<td>1.47 (±0.02)</td>
</tr>
<tr>
<td>2-Picoline</td>
<td>17.0</td>
<td>18.5</td>
<td>16.1</td>
<td>1.22 (±0.03)</td>
</tr>
<tr>
<td>3-Picoline</td>
<td>17.9</td>
<td>18.6</td>
<td>15.1</td>
<td>1.38 (±0.02)</td>
</tr>
<tr>
<td>4-Picoline</td>
<td>17.2</td>
<td>18.2 (±0.2)</td>
<td>14.6</td>
<td>1.36</td>
</tr>
<tr>
<td>2,3-Lutidine</td>
<td>15.6</td>
<td>18.9</td>
<td>12.8</td>
<td>1.49 (±0.02)</td>
</tr>
<tr>
<td>2,4-Lutidine</td>
<td>17.6</td>
<td>22.4</td>
<td>16.4</td>
<td>1.25$^c$</td>
</tr>
<tr>
<td>2,6-Lutidine</td>
<td>19.4</td>
<td>21.9</td>
<td>18.0</td>
<td>1.47$^c$</td>
</tr>
<tr>
<td>2,4,6-Collidine</td>
<td>17.6</td>
<td>18.6 (±0.2)</td>
<td>14.6</td>
<td>1.20$^c$</td>
</tr>
<tr>
<td>Quinoline</td>
<td>15.2</td>
<td>20.8</td>
<td>13.7</td>
<td>1.45$^c$</td>
</tr>
<tr>
<td>Isoquinoline</td>
<td>16.2</td>
<td>17.2</td>
<td>12.5</td>
<td>1.22$^c$</td>
</tr>
<tr>
<td>Piperidine</td>
<td>19.7 (±0.2)</td>
<td>25.5 (±0.3)</td>
<td>14.6</td>
<td>1.10$^c$</td>
</tr>
<tr>
<td>Pyridine–cyanuric acid compound</td>
<td>16.0</td>
<td>21.7</td>
<td>17.5</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Accurate to ±0.1 g/ml, except as noted.
$^b$Accurate to ±0.01 g/ml, except as noted.
$^c$These values determined only on toluene-washed samples.
TABLE 6. CHEMICAL COMPOSITION OF SUBSTITUTED PYRIDINE–BORIC ACID COMPOUNDS$^a$

<table>
<thead>
<tr>
<th>Base</th>
<th>$\text{B}_2\text{O}_3$ (moles/mole of base)</th>
<th>$\text{H}_2\text{O}^b$ (moles/mole of base)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Picoline</td>
<td>2.1</td>
<td>3.5</td>
</tr>
<tr>
<td>3-Picoline</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>4-Picoline</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>2,3-Lutidine</td>
<td>2.8</td>
<td>4.6</td>
</tr>
<tr>
<td>2,4-Lutidine</td>
<td>2.4</td>
<td>3.1</td>
</tr>
<tr>
<td>2,6-Lutidine</td>
<td>12</td>
<td>33</td>
</tr>
<tr>
<td>2,4,6-Collidine</td>
<td>2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Quinoline</td>
<td>5.7</td>
<td>7.5</td>
</tr>
<tr>
<td>Isoquinoline</td>
<td>2.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Piperidine$^c$</td>
<td>2.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$^a$Toluene-washed.
$^b$Karl Fischer method; corrected for $\text{B}_2\text{O}_3$ content.
$^c$Analysis corrected; based on fact that piperidine is a strong base.

The 17 to 19 Å spacing found in all the compounds but two (Table 5) is taken to be six times the interlayer spacing in HBO$_2$(III) (3.12 Å). Since each pyridine ring has a unique direction, there are three different orientations relative to a parallel B$_3$O$_3$ ring which, taken with the fourfold symmetry required by the HBO$_2$ structure, account for the presence of six layers per unit cell in the compounds, as opposed to two layers in the original acid. The structure is then made up of alternate sheets of HBO$_2$ and organic base. The electronic structure of the B$_3$O$_6^{2-}$ ion is similar to that of the isoelectric ion of cyanuric acid, C$_3$N$_2$O$_3^{2-}$, and the crystal structure$^4$ of cyanuric acid is very similar to that of HBO$_2$(III). Pyridine has also been found to react readily with cyanuric acid, yielding a product with an x-ray diffraction pattern very similar to that of the pyridine–boric acid compound.

REACTOR EXPERIMENTS

EFFECT OF RADIATION ON ANALYSIS OF CHROMIUM, IRON, AND NICKEL

W. E. Browning        R. P. Shields

On numerous occasions, corrosion, as indicated by chemical analysis of a radioactive fuel, has shown inconsistent results. This has raised the question of the possibility that the analysis is being affected by radiation from the fission products in the sample.

A study is under way for the purpose of determining whether there is a radiation effect, and if so, to what extent. Preliminary spectrophotometric tests of a sample of chromium in the presence of a high-intensity beta source have indicated that the radiation may cause a high value for the chromium. In another test, where hydrogen peroxide was introduced into the sample, a slow decrease in the amount of light transmitted in the spectrophotometer was also indicated; this would also give a high value for chromium. These tests and others are now being carried out under more exacting conditions, with carefully prepared control samples, and all the variables pertaining to the tests will parallel those involved in the testing of actual fuels.

HOLDUP OF FISSION GASES BY CHARCOAL TRAPS

W. E. Browning
Solid State Division
D. E. Guss
U. S. Air Force

A series of charcoal traps of different geometries but having the same amount of charcoal are being tested in radiokrypton holdup experiments. Nitrogen purge gas is being used at various temperatures below room temperature. The results of these tests will aid in extending, to traps of different shapes, the relationships reported earlier.\(^1\) The work described earlier has been formulated into a report\(^2\) and issued.

\(^1\)W. E. Browning and C. C. Bolto, ORNL-2061 (March 10, 1956) (Secret).

TECHNIQUES AND EQUIPMENT UTILIZED IN LOW-TEMPERATURE REACTOR IRRADIATIONS

T. H. Blewitt  T. S. Noggle
R. R. Coltman  C. E. Klabunde

Early attempts to describe the basic nature of radiation damage were based upon the measurement of the physical changes which occurred in materials that had been bombarded at or near room temperature. Almost at the outset of research in this field, it was recognized that some radiation-induced defects might be mobile below room temperature. Observation of these defects could be made only if they were frozen into the material during bombardment and subsequently studied under controlled low-temperature conditions.

The bombardment and study of materials at or near liquid-nitrogen temperature were successfully accomplished by workers at ORNL and other laboratories. The results of this work clearly established the existence of defects mobile at low temperature and showed that the effect of these defects on certain physical property characteristics was at least equal in magnitude to the effects produced by room-temperature bombardments. In addition to these data, the results of some low-temperature irradiations made at ORNL implied that bombardment of materials at still lower temperatures was necessary if the nature of radiation damage was to be completely studied. Calculations were made with regard to the amount of refrigeration required in order to bombard specimens near $20^\circ$K. The results, from a number of viewpoints, showed that the machinery required was not practical. It was discovered, however, that a number of helium refrigerators used in another AEC program had become surplus. It was clear that these devices were adaptable to reactor-bombardment work, and one was acquired by ORNL for this purpose. The machine was modified by the Arthur D. Little Company. This modification satisfied the requirements of increased capacity, constant temperature control ($\pm 10^\circ$K), and improved reliability. After modification, the measured heat capacity was 300 w at $21.5^\circ$K. On the basis of subsequent operating experience, however, it is believed that the machine is presently being run under more nearly optimum conditions and that the capacity is near 500 w at this temperature. Because of the fast-neutron flux in the reactor facility available for these experiments, reliability is an important requirement. It was felt that an uninterrupted low-temperature bombardment of one week would be necessary in order to obtain large enough changes in the materials to permit a detailed study. At the present time, 15 nonstop 180-hr runs and one 360-hr run have been made; and a total running time of 4000 hr has been accumulated with only minor difficulties. A detailed description of the operating principles of the refrigerator has been given by Pastuhov. A helium as a refrigerant is particularly adaptable to reactor work, since it does not become radioactive.

Cryostat Construction

The facility available for these experiments in the ORNL Graphite Reactor has a fast-neutron flux of $7 \times 10^{11}$ neutrons-cm$^{-2}$-sec$^{-1}$ and consists of a vertical telescoping hole (No. 12) whose minimum cross section is 4 in. square. The distance from the top to the center of the reactor (region of highest neutron flux) is about 20 ft. The design considerations for a cryostat in this facility led to several, more or less complicated, configurations. The use of a liquid-nitrogen-temperature shield was temporarily abandoned because of space limitations. It was felt that simplicity would be the most expeditious approach. In view of this, the cryostat was designed in four principal parts: a sample tube leading to the sample chamber, a combination sample chamber and heat exchanger, inlet and outlet helium lines, and a vacuum jacket which houses the entire assembly and serves as the only insulator. Figure 32 is a schematic drawing of the cryostat, with an outline sketched to scale at the right of the figure. A cardinal rule of reactor research states that any object which goes into a reactor must be removable. For this reason aluminum was chosen as a construction material for the cryostat, since it has a short-lived radioactivity, and relatively large masses of

---

Fig. 32. Schematic Diagram of Hole No. 12 Cryostat.

it may be removed from the reactor, without shielding, several hours after the reactor is shut down. It was estimated that, for any other suitable construction material, the cost of a removal shield for personnel protection against radioactivity would exceed the cost of the cryostat. Consequently, the lower 17 ft of the cryostat is made entirely of 2 S aluminum, except for a few small fired-Lavite pins, which serve as spacers. Since the upper end of the aluminum sample tube was at room temperature and the lower end below 20⁰K, a heat trap had to be incorporated, as shown in Fig. 32. (The aluminum-to-silver joint was developed by R. J. Fox of ORNL.) The two metals were joined in air by using eutectic No. 190 aluminum brazing alloy with copious amounts of flux and an induction heater. The operation must be completed quite rapidly, since the brazing alloy dissolves both metals. The joint is mechanically strong and vacuum-tight but is susceptible to corrosion in air. Since the helium lines in the refrigerator are copper, it was necessary to make the joints for each of these in the same way (see Fig. 32). Since the gas tubes cool down faster and are cooler than the entire length of the sample tube at all times, and since all three tubes are anchored both at the top and the bottom of the cryostat, it was necessary to allow for differential expansion between them. This was accomplished by placing 1-ft sections of flexible stainless steel hose in the annulus of a double-walled can, which was thermally isolated from both the sample tube and the vacuum jacket. The arrangement can be noted in Fig. 32. The gas tubes are free to slide in and out of the double-walled can without plastically deforming the hose. The observed differential expansion is about 1/2 in. Figure 33 shows a

Fig. 33. Sample Chamber-Heat Exchanger with the Pressure Jacket Removed.
photograph of the sample chamber—heat exchanger with its pressure jacket removed. It was machined from a solid rod of aluminum and consists of a double-threaded helix with a $1\frac{3}{4}$-in. hole through the center. The incoming gas travels down one thread, crosses over at the bottom, and returns up through the other thread. The pressure jacket slip fits over the double helix and is welded around the top. The usable length of the sample chamber is 24 in. The inner assembly and inside wall of the vacuum jacket were bright-dipped so as to reduce thermal-radiation losses.

G. Fielder of ORNL contributed many valuable suggestions and assisted in the building of the apparatus for these experiments, particularly the hole No. 12 cryostat.

**Equilibrium Sample Temperature**

The gamma radiation created inside the reactor causes uniform heating of materials through which it passes. The amount of heating in this facility is 4.7 mw/g or about 2 w/lb. With the reactor at full power, the refrigerator can maintain the wall of the sample chamber at 10–11°C K. The heat that is generated in specimens inside the sample chamber is transferred to the walls by the helium exchange gas. The equilibrium sample temperature may be described by the following simple argument:

\[
\frac{dQ_{in}}{dt} = \frac{dQ_{out}}{dt} ,
\]

or

\[
y = kS \left( T_w - T_s \right) ,
\]

where \( y \) is the gamma-ray heating constant in w/g, \( m \) is the sample mass, \( k \) is a convection constant or heat-transfer constant in w/cm²·deg and is a function of the exchange-gas pressure, \( S \) is the surface area, \( T_w \) is the wall temperature, and \( T_s \) is the sample temperature. On substituting \( \rho V \) for \( m \), where \( \rho \) is the sample density and \( V \) is its volume, Eq. 2 becomes:

\[
T_s = T_w - \frac{\gamma \rho V}{kS} .
\]

It can be shown that, for samples with reasonable volume-to-surface ratios (i.e., \( \frac{1}{8} \)-in. rods), heat losses due to thermal radiation from the sample to the wall may be ignored at operating temperatures. With an exchange-gas pressure of 1 atm and with the reactor at full power, \( \frac{1}{8} \)-in. rods of copper (density = 9 g/cc) reach an equilibrium temperature of about 15°C K. It is believed that samples with very small volume-to-surface ratios (i.e., thin foils) would very nearly reach the wall temperature under the same conditions.

Two techniques used in various experiments in the hole No. 12 cryostat may be of interest.

**The Use of Gamma Radiation for Stored-Energy Measurements**

It was desired to measure the energy stored in copper and aluminum after a low-temperature bombardment in the cryostat. The following method is particularly adaptable to this experiment. If \( C_p \) refers to the specific heat of a material in its normal state (the material contains no stored energy), then

\[
C_p \frac{dT}{dt} = \frac{dQ}{dt} + \frac{dE}{dt} ,
\]

where \( Q \) is external heat added to the sample, and \( E \) is the stored energy. If external heat is supplied to the sample at a constant rate, \( \frac{dQ}{dt} = \gamma \), then

\[
C_p \frac{dT}{dt} = \gamma dt + \frac{dE}{dt} ,
\]

or

\[
\frac{dt}{dT} = \frac{1}{\gamma} \left( C_p - \frac{dE}{dT} \right) .
\]

Now, consider that a sample containing stored energy undergoes two consecutive warmup operations, with the same constant rate of external-heat input \( \gamma \) in each case. It is assumed that the stored energy is thermally activated and released during the first run and is not present in the second run. During each run the temperature of the specimen and the time are recorded. By computing the slopes of the resulting curves, values for \( \frac{dt}{dT} \) as a function of \( T \) may be obtained. Since there is no stored energy in the second run (\( \frac{dE}{dT} = 0 \)), the two sets of values for \( \frac{dt}{dT} \) will be different. Consequently, for the first run,

\[
\frac{dt}{dT} = \frac{1}{\gamma} \left( C_p - \frac{dE}{dT} \right) ,
\]
and for the second run,

\[
\frac{dt}{dT} = \frac{C}{\gamma}.
\]

On subtracting and solving for \(dE\), the following expression results:

\[
dE = \gamma \left[ \frac{dt}{dT} - \frac{dt}{dT}\right] dT.
\]

The stored energy released in any temperature interval may be found by integrating Eq. 9. This may best be done graphically by determining the area underneath each of the two curves \(\gamma \frac{dt}{dT}\) vs \(T\) and \(\gamma dt/dT\) vs \(T\).

It should be noted that the method above is valid only if the heat, \(\gamma\), is supplied to the sample in such a way that thermal gradients in the sample do not exist at any time; that is, the heat must be supplied homogeneously throughout the entire volume of the sample.

One method employed for measuring stored energy at low temperatures consists of (1) supplying a known quantity of heat to the sample externally, (2) waiting for thermal equilibrium, and (3) measuring the resulting temperature rise. A value for an apparent specific heat can then be computed from these data; and by comparison with the normal specific heat of the sample, the stored energy can be found. The specific heats obtained in this manner, however, are only average values for the temperature intervals involved, and this is a limitation that is not imposed by the method described above.

In the experiments described here, it was necessary that all measurements be made inside the cryostat. It was assumed that the reactor gamma radiation would serve as an excellent heat supply, since it would meet the requirement of homogeneity imposed by the method outlined above for the measurement of stored energy.

It is particularly important in experiments of this type to ensure good thermal isolation of the sample from its surroundings during the warmup runs. It can be shown that the heat loss from the sample, due to thermal radiation during a warmup run, is small compared to the sensitivity required in the experiment. The maximum temperature reached during a run was 600K, with the cryostat wall maintained at 100K. In the early experiments, the sample was kept cold during a bombardment by using about 1 atm of helium exchange gas in the sample chamber. After bombardment and with the reactor off, the exchange gas was pumped out of the sample chamber in an effort to thermally isolate the sample from the chamber walls. It was found, however, that complete isolation could not be achieved. It is believed, because of the low temperature and the long time of bombardment, that a considerable amount of helium was adsorbed on the surface of the specimen and was only very slowly removed, even when high-speed pumps were employed.

Satisfactory results were obtained, however, by use of the scheme shown in Fig. 34. Samples used for these experiments were in the form of a pillbox \(\frac{3}{4}\) in. in outside diameter and \(\frac{1}{2}\) in. in length. A combination of mechanical contact of the sample with the bottom of the chamber and helium exchange gas at low pressure served to cool the sample during bombardment. It has been observed by Berman\(^2\) that heat transfer by mechanical contact at low temperatures varies


![Fig. 34. Schematic Diagram of Apparatus for Measurement of Specific Heat, as Installed in Hole No. 12 Cryostat.](image-url)
directly as the total contact force. So as to reduce to a minimum the amount of exchange gas required to properly cool the sample, a 10-lb lead weight was used to press the sample against the bottom of the chamber. The weight was located above the reactor lattice so that it would not be heated by gamma radiation. As can be seen in Fig. 34, raising the 10-lb weight first disengages the pushrod from the sample and then raises the sample off the bottom of the cryostat so that it is supported only by a No. 30 copper-constantan thermocouple embedded in the center of the sample. The experimental procedure was as follows:

1. The sample was placed in the cryostat and the lead weight was lowered against it. The sample chamber was then evacuated.

2. The cryostat was cooled down to terminal temperature and the reactor was turned on.

3. Since mechanical contact alone was not sufficient to maintain a desirable bombardment temperature (about 20°K) with the reactor at full power, a small amount of helium exchange gas (usually about 25 μ) was introduced into the sample chamber until the sample cooled back down to this temperature. The chamber was then sealed off for the one-week bombardment.

4. After the bombardment and with the reactor turned off, the exchange gas was removed by pumping on the sample chamber for about 6 hr. The mechanical contact alone was sufficient to maintain the sample below 20°K with the reactor off or operating at low power levels. (When the reactor is off, there is sufficient residual radiation to cause noticeable heating of thermally isolated samples at these low temperatures.)

5. The reactor was then turned on and brought up to one-tenth full power. The sample was then raised out of contact with the cryostat and heated by the gamma rays. A temperature-time curve was recorded.

6. Upon reaching about 60°K, the sample was lowered again into the bottom of the cryostat and allowed to cool back to 20°K. A second temperature-time curve was then taken according to the same procedure.

So as to ensure that the gamma heating was constant at the location of the cryostat in the reactor, a neutron fluxmeter was inserted into the reactor adjacent to the cryostat. During the warm-up runs, this device was used to hold the power level of the reactor to within 1%, instead of using the normal reactor-power-level monitor. About 80 min at one-tenth full reactor power was required to warm a sample from below 20°K to 60°K. In order to determine the value of the gamma-ray heating, it was necessary to normalize the curves of $dt/dT$ vs $T$ at one point with the specific-heat data of Giauque and Meads. The resulting dependence of $C_p$ on $T$ was found to be in excellent agreement with that of Giauque and Meads. This is illustrated in Fig. 35, which shows the curves of $dt/dT$ vs $T$ computed from two consecutive warmup runs from a stored-energy experiment on aluminum. It may be noted from the area between runs A and B, shown in Fig. 35, that the stored energy released in aluminum after a low-temperature bombardment is very small up to 60°K. A complete report and analysis of the results of these experiments is to be published.

![Graph showing specific-heat data for aluminum](image)

**Fig. 35.** Specific-Heat Curves of Aluminum, as Derived from Two Consecutive Warmup Runs After Low-Temperature Bombardment in Hole No. 12 Cryostat.

**The Condenser-Discharge Method for Pulse Annealing**

The resistivity changes induced in several metals by low-temperature neutron bombardment have been studied at ORNL. The temperature coefficient of many of these materials changes...

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4Submitted to American Society of Metals Seminar, Oct. 1956.
rapidly in the region of 20 to 80°K. In addition, many of the metals were of high purity and had relatively low residual resistivities. In order to examine the annealing properties of the resistivity induced by the bombardment, it was necessary that all measurements be made at some low reference temperature (about 15°K), where changes only in residual resistivity are observed and where the thermal component of resistivity is negligible. Experiments involving both isothermal-annealing and tempering curves were made. Since resistance measurements could not be made at elevated temperatures, it was necessary to pulse the specimens from a reference temperature to the desired temperature, hold them for a given time at the desired temperature, and then quench them back to the reference temperature. The analytical accuracy of the data depends upon the squareness of the pulse. The method of pulsing, which is suitable for work in the laboratory as well as in the reactor, employed the discharge of condensers through a heater.

A number of specimens were mounted inside a vacuum-tight copper can, along with a 50-ohm Nichrome heater wound on a fired-Lavite form. All leads were brought up through a thin-walled stainless steel tube to the top of the cryostat and out through vacuum-tight seals. The can was thermally isolated from the cryostat wall by mechanical means, then filled with helium exchange gas, and sealed off. Exchange gas was also introduced into the sample chamber during bombardment so that gamma-ray heating, induced in the specimens, could be transferred to the cold wall of the cryostat. By this scheme, samples could be bombarded at about 17°K. After bombardment and with the reactor off, the exchange gas in the sample chamber was pumped out, whereas that in the copper can remained to serve as a heat-exchange medium between samples, thermocouple, and heater. With the can thermally isolated from the cryostat, an electrical pulse from a bank of condensers was discharged through the heater. The maximum temperature attained in the can was held (±0.1°K) for the period of pulse by means of a small current (manually controlled) through the heater. At the end of the period the current was turned off, and helium exchange gas was reintroduced into the sample chamber, which quenched the can back to the reference temperature. Figure 36 shows a typical assembly used in this type of experiment. The mass of the complete assembly is about 300 g. Condensers were arranged in steps of 1000 µf up to a total of 50,000 µf. When charged to 141 v, the total capacitance stored 500 w/sec of energy, which was sufficient to raise the can from 17 to 60°K. By means of trial runs before bombardment, a curve of capacitance vs pulse temperature could be made. The curve could then be used to obtain any desired pulse temperature up to 60°K after the bombardment. After an initial isothermal pulse, it was found that the temperature of succeeding pulses could be reproduced to within 0.1°K. The time required to reach equilibrium at a particular pulse temperature was about 20 sec, with about half this time being consumed in attaining the last few degrees, where new annealing might conceivably start. The time required to quench back to the reference temperature was several minutes; however, half of the temperature drop was accomplished in less than 5 sec.

The condenser-discharge method is a simple one to use, since only the voltage across a given set of condensers has to be monitored in order to obtain reproducible temperature pulses. Within reasonable limits the reproducibility of pulses is independent of changes in heater resistance as a result of temperature or different size heaters. A Simplytron meter-relay, wired as a voltmeter across the condensers and operating a standard relay, served to switch the condensers from charge to discharge always at the same preset voltage (about 141 v).

Copper-constantan thermocouples were checked against a gas thermometer in the cryostat, and it was found that their calibration did not change after a one-week bombardment. All thermocouples used in these experiments were calibrated against a standard platinum resistance thermometer before being used.

The Hazard of Cryogenic Apparatus in Radiation Fields

There have been two explosions of cryogenic devices inside the graphite reactor at ORNL. In the first explosion, the device consisted of an open-mouthed aluminum Dewar 22 ft in length which was filled with liquid nitrogen. The incident occurred after three days of operation in the reactor and was immediately followed by an intense odor of ozone in the vicinity.
The second explosion occurred during the initial run of the cryostat described in this paper. The vacuum line leading to the sample tube ruptured. Several hours elapsed before repair could be made, and air froze in the sample chamber. During warmup, after termination of the run, the cryostat exploded. A new cryostat was built; a few salvaged parts from the old one were used, and certain safety devices were added.

It is believed that in each incident a large fraction of the oxygen which condensed in the cryostat was immediately converted to ozone by the ionizing radiations of the reactor. The exact nature of the explosive reaction is not known, but several

Fig. 36. Assembly for Measuring Resistivity Changes in Hole No. 12 Cryostat.
possibilities are the sudden decomposition of ozone, a nitrogen-ozone reaction, or the reaction of ozone with small quantities of foreign organic material. It is firmly believed that small quantities or concentrations of liquid or solid oxygen in the presence of intense ionizing radiations constitute a hazardous condition.

MECHANISM OF ANNEALING IN NEUTRON-IRRADIATED METALS
T. H. Blewitt D. K. Holmes
R. R. Coltman T. S. Noggle

Introduction
The effect of nuclear radiation on the properties of solids has received considerable attention since E. Wigner\(^5\) correctly forecast that such effects would have important consequences in reactor design. Research on radiation damage was initiated after the ORNL Graphite Reactor was in operation, and the investigations were primarily concerned with solving problems arising from radiation effects in the reactor materials themselves.

Since 1947, research in the field has increased, and it has been characterized by an improvement in the experimental techniques. Metals and alloys have been quite extensively investigated, and the data have yielded a better insight into the mechanism by which reactor irradiations affect the physical properties of solids. The temperature instability of radiation-induced defects has necessitated the employment of low-temperature irradiations to freeze in all defects, particularly in experiments that are designed to provide further information pertaining to the fundamental mechanism of radiation damage. From a theoretical standpoint, important new concepts regarding the mechanism of the production and the migration of radiation-induced defects have been introduced. Brinkman\(^6\) has introduced the displacement spike; Kinchin and Pease\(^7\) have proposed the concept of interstitialcy migration; and Lomer and Cottrell\(^8\) have presented a new defect, the crowding of point defects. Computations, improving on the original calculations of Seitz,\(^9\) have been made by Snyder and Neufeld,\(^10\) as well as Seitz and Harrison.\(^11\)

Most recently, attention has been focused on experiments concerned with the changes in resistivity that are associated with bombardments at very low temperature, that is, in the range 10 to 20°K. The manner in which this enhanced resistivity changed while the sample was heated to room temperature has been of particular interest. In fact, finding an explanation for the resultant recovery of the electrical resistivity has been of interest to researchers in the field of radiation damage during the past few years. The extreme scarcity of available data has led to a situation in which the number of explanations approaches the number of scientists actively engaged in the field of radiation damage. It is the purpose of this paper to evaluate the various interpretations of the annealing spectrum for a solid material which arises as a result of low-temperature irradiation.

Theoretical Considerations
An adequate survey of the theoretical aspects of radiation effects has been made in a recent review article by Seitz and Koehler.\(^12\) These effects have been studied experimentally by the utilization of three types of irradiation: fast neutrons from nuclear reactors, heavy charged particles from cyclotrons, and energetic electrons from Van de Graaff generators. A brief non-mathematical description of the effect of a fast neutron (one whose energy is about 1 Mev) striking a metal of intermediate or heavy atomic weight (say Z ≥ 25) will provide a valuable background for the subsequent discussion of the experimental work. Consider, according to the theoretical physicists, what will happen when a neutron strikes a metal such as copper. Since the neutron carries no charge, it will easily be able to penetrate metals. To a first approximation, it can only interact with the metal by directly striking

the nucleus of an atom in a billiard-ball-type collision. Since the area of the nucleus which presents itself as a target to the neutron is exceedingly small, a neutron will only strike about one atom as it passes through an average-size laboratory sample (1 cm). This struck atom, referred to as a primary knock-on, will be ejected from the lattice with a kinetic energy that can be determined from the laws of classical physics. For a fission neutron, that is, one whose energy is the order of 1 Mev, the primary knock-on will receive an energy of about 60,000 ev. The majority of this energy will be dissipated in the form of heat, with the remainder forming lattice defects. At the beginning of the range, when the primary knock-on is traveling fast, it will be relatively uninfluenced by the outer orbital electrons of the lattice atoms so that its energy will be mainly dissipated as a result of coulomb interaction between its ion core and the ion cores of the atoms forming the metallic lattice. The resulting agitation, which is equivalent to thermal agitation, is called a thermal-spike region. As the lattice absorbs energy from the displaced atom, the velocity of the knock-on decreases, and the outer orbital electrons of the lattice will effectively screen the coulomb fields of the nuclei. The atoms will then appear as hard spheres to the displaced atom, and collisions more representative of the billiard-ball type will result. The agitation resulting from this lattice process, which is again similar to thermal agitation, is known as a displacement spike. The net result of both these processes will be to raise the temperature of several thousand atoms a few thousand degrees Kelvin for a period not exceeding $10^{-10}$ sec. In addition to this thermal agitation resulting from the displaced atom, the primary knock-on may transfer enough energy to some of the lattice atoms along its path to displace them from their lattice sites. These are called secondary knock-ons. In the case of fission neutrons, it is believed that secondary knock-ons have sufficient energy to cause further displacements, called tertiary knock-ons. The net result of this second effect will be the production of a number of displaced atoms which leave lattice sites vacant and create interstitial atoms when they finally come to rest. It is calculated that an average fast neutron in a thermal reactor will produce about 100 of these secondary and tertiary displacements per neutron hit.

In the case of bombardment of metals by charged particles from a cyclotron, there is little difference in the events described above for neutron irradiation, with the exception that the incoming particles, usually deuterons or alpha particles, dissipate a large fraction of their energy by electronic excitation. (The primary knock-on in neutron irradiation will also lose energy by electronic excitation, but for the metals which have a $Z \geq 25$ this will be small.) The energy of the primary knock-on for charged-particle bombardment is usually considerably smaller than that for fission neutrons; and in the normal case, the energy does not exceed a few hundred electron volts. Hence, the displacement-spike phenomenon will predominate over the thermal-spike phenomenon, and it will be of smaller size and intensity than in the case of reactor bombardment.

Electron bombardment is usually carried out with electrons of just sufficient energy (about 1 Mev) to produce primary knock-ons. This type of bombardment will thus differ from cyclotron and reactor bombardments in that the displacement and thermal spikes will be of negligible importance. Thus, only those effects attributable to the defects themselves will be evident.

**Determination of the Number of Defects Produced During Irradiation**

One of the foremost problems in the past few years has been the experimental verification of the calculations of the number of interstitial atoms and lattice vacancies produced by a neutron hit (one interstitial atom and one vacant lattice site are sometimes called a Frenkel pair or a Frenkel defect). For the most part the experimental technique has involved the measurement of the irradiation-induced change in the electrical resistivity; and this, coupled with the theoretical estimate of the electrical scattering cross section of a Frenkel pair, leads to an estimate of the number of Frenkel pairs per neutron hit. Unfortunately, it has not been possible to experimentally determine the scattering cross section. These attempts to determine the defect density have not been satisfactory. Scattering factors, calculated according to theory, have shown a wide divergence. For example, Jongenburger\(^{13}\) refined the results of

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Dexter\textsuperscript{14} and obtained a scattering factor of 1.3 μohm·cm for 1 at. % of vacancies. Blatt\textsuperscript{15} made a similar computation for interstitial atoms and arrived at 1.4 μohm·cm per atomic per cent of interstitials. Recently Overhauser and Gorman\textsuperscript{16} pointed out that Blatt's computation did not take into account the strain field around the interstitial atom; their results, which included the increase in scattering due to the strain field, raised the estimate of the scattering cross section of an interstitial atom to about 9 μohm·cm/at. %. Overhauser and Gorman have thus demonstrated that the strain caused by an interstitial atom can have far-reaching effects on the magnitude of the resistivity change. At the present time, it is not clear how the relaxation of the strains will occur about an interstitial atom. In view of the uncertainty as to the exact nature of the relaxation, it would appear that the calculated results for the scattering factor cannot be taken too seriously.

Snyder and Neufeld\textsuperscript{10} have made theoretical calculations on the number of displacements per neutron hit as a function of the incident neutron energy. For the flux distribution in hole No. 12 in the ORNL Graphite Reactor, Snyder and Neufeld's theory leads to an estimate of about 110 displacements per neutron hit.

The experimentally determined change in electrical resistivity of high-purity-copper single crystals irradiated at 22K in the hole No. 12 cryostat is shown in Fig. 37. From the known neutron elastic-scattering cross section and by use of Jongenburger's and Blatt's values for the electrical scattering factor per Frenkel pair, the data in Fig. 37 give an estimate of about 20 displacements per neutron hit. This estimate drops to about five per hit if Gorman and Overhauser's value for the scattering factor of the interstitial atom is used instead of Blatt's. It is thus seen that, even if the entire resistivity change is attributed to Frenkel pairs, the number estimated from resistivity measurements is smaller by a factor of 5 than the theoretical number, even if the most favorable electron-scattering cross section is used.

The analysis of radiation-induced resistivity, as a result of cyclotron bombardment at low tem-

perature, leads to the same conclusion; that is, the number of defects per primary displacement, as deduced from Blatt's and Jongenburger's theoretically determined scattering factors and from the change in resistivity, is too small by a factor of about 5 when compared with the number expected from theory. At present, the results of electron bombardment at low temperature yield inconclusive results, since the probability of a displacement will strongly depend on (1) the threshold energy needed to displace an atom and (2) the shape of the well. Neither of these is well understood at present.

The study of the effect of low-temperature reactor irradiation on the electrical resistivity has been extended to include several metals and alloys. Figure 38 summarizes the results for the different metals. It may be concluded that these data are representative, since at least two subsequent bombardments were made and identical results were obtained. The extent of the reproducibility can be judged from Figs. 39, 40, and 41. It should be noted that for all the metals the change in resistivity is directly proportional to the neutron flux, indicating the absence of radiation annealing. It can thus be inferred that there is only slight, if any, interaction between adjacent damaged regions.

It is not clear why the various metals on being subjected to a neutron flux show such a drastic difference in their rate of change of electrical resistivity. There does not seem to be any correlation between the lattice structure, Debye temperature, neutron elastic-scattering cross section, atomic weight, dislocation density, purity, initial resistivity, and outer shell electrons. A further understanding of the process will be required before it can be decided whether this difference in behavior is the result of a different resistivity scattering cross section per defect or a variation in the number of defects per neutron hit, or both.

Recovery of the Resistivity of Reactor-Irradiated Metals

The relatively crude annealing data of cyclotron-irradiated copper clearly showed that radiation-induced resistivity recovered at temperatures as low as 40°K. An annealing spectrum of irradiated copper bombarded at 18°K in the hole No. 12

\textsuperscript{14} D. L. Dexter, Phys. Rev. 87, 768 (1954).
\textsuperscript{16} A. W. Overhauser, private communication.
Fig. 37. Effect of Neutron Bombardment at 22.4°C on the Resistivity of Copper Single Crystals.

cryostat is shown in Fig. 42. This annealing spectrum, which is typical of many metals, has been the source of considerable speculation. The tempering curve of Fig. 42 can be interpreted as the result of three distinct processes. One process is evident in the temperature range from 30 to 50°C (process I); a second process occurs in the region from 50 to 240°C (process II); and a third occurs in the region from 240 to 300°C (process III). A fourth process occurring in the region from 600 to 900°C, which strongly affects the mechanical properties, has also been found (process IV).

\[ \text{FAST FLUX} = 7 \times 10^{11} \text{neutrons cm}^{-2} \cdot \text{sec}^{-1} \]

BOMBARDMENT TEMPERATURE 22.24 ± 0.32°C

- **SAMPLE 382 C**
  - \( \rho_0 = 6.00 \times 10^{10} \text{ohm-cm} \)
  - \( \rho_{22.24} = 1.970 \times 10^{-9} \text{ohm-cm} \)

- **SAMPLE 354 F**
  - \( \rho_0 = 2.995 \times 10^{-9} \text{ohm-cm} \)
  - \( \rho_{22.24} = 4.365 \times 10^{-9} \text{ohm-cm} \)

\( nvt_f \), INTEGRATED FLUX (fast neutrons/cm²)
Fig. 38. Effect of Neutron Bombardment on the Resistivity of Several Metals. No correction has been applied to these data for temperature fluctuations.

The annealing spectrum\textsuperscript{18} of copper samples irradiated by deuterons at 10 to 200K is very similar to those described above, as can be seen in Fig. 43. Since these samples were warmed up without any control, the details of Fig. 43 may appear different from the details of Fig. 42. However, there can be little doubt that processes I, II, and III are present. Other data also show the presence of process IV. In order to ascertain the effect of thermal and displacement spikes, it would be very interesting to compare those spectra arising from a warmup of low-temperature deuteron- and neutron-bombarded specimens with that arising in specimens after low-temperature electron bombardment. Denney and co-workers\textsuperscript{19} have recently examined the annealing, in the temperature range from 10 to 800K, of the resistivity induced in copper by irradiation at 5 to 100K with 1.3-Mev electrons. They found a process similar to that which has been termed process I; however, the fraction of resistivity which appears to anneal at this temperature is greater than that which occurs upon warmup after low-temperature neutron and deuteron bombardment. Meechan and Brinkman,\textsuperscript{20} on the other hand, have examined the annealing spectrum of copper bombarded at 800K with 1-Mev electrons. According to them, a spectrum results which indicates that annealing processes II and III are occurring. It is thus apparent, since processes I, II, and III are present in low-temperature neutron, deuteron, and electron bombardment, that the displacement spike or the


\textsuperscript{20}C. J. Meechan and J. A. Brinkman (in press).
Fig. 39. Effect of Neutron Bombardment on the Resistivity of National Research Corp. Iron. Bombardment temperatures were as follows: run 1, $14.5 \pm 1.5^\circ$K; run 2, $14.5 \pm 1.5^\circ$K; run 3, $17.6 \pm 0.8^\circ$K; run 4, $19.3 \pm 1.8^\circ$K. No correction has been applied for temperature fluctuations; and at the last point of each run, the measured resistivity is too small, since the temperature falls about $4^\circ$K when the reactor is turned off.

Fig. 40. Effect of Neutron Bombardment on the Resistivity of 99.996% Aluminum. Bombardment temperatures were as follows: run 1, $14.5 \pm 1.5^\circ$K; run 2, $13.8 \pm 0.8^\circ$K; run 3, $17.6 \pm 0.8^\circ$K; run 4, $19.3 \pm 1.8^\circ$K. The experimental points are not corrected for temperature.

Fig. 41. Effect of Neutron Bombardment on the Resistivity of National Research Corp. Nickel and of Mond-Process Nickel. Bombardment temperatures were as follows: run 1 (NRC nickel), $14.5 \pm 1.5^\circ$K; run 2 (Mond nickel), $13.8 \pm 0.8^\circ$K.

Fig. 42. Annealing Spectrum of Reactor-Irradiated Copper. The zone-refined copper sample was bombarded at $17.5 \pm 1^\circ$K to a total of $8 \times 10^{17}$ neutrons. The resistivity at each point on the curve was measured at $14^\circ$K following a 3-min pulse at this indicated temperature.
Fig. 43. The Decrease of Bombardment-Induced Resistivity of Copper, Silver, and Gold as the Samples Are Warmed Slowly from Liquid-Helium Temperatures. (See ref 18.)

thermal spike in themselves cannot play a predominant role in damaging the sample in so far as the low-temperature-annealing peaks in electrical resistivity are concerned.

In the subsequent paragraphs of this article, each of these annealing processes will be examined in detail, and various interpretations will be critically examined.

Migration by an Interstitialcy Process

Siegel\textsuperscript{21} discovered that neutron bombardment of an initially ordered specimen of Cu\textsubscript{3}Au caused a disordering reaction to occur. The number of atoms necessary to the interchange, in order to explain the observed rate of disorder, greatly exceeded the calculated number of displacements. This disordering was initially attributed to thermal spikes, but subsequent considerations indicate that the time duration of the spike and its energy are not sufficient to account for the observed disordering.

In order to explain this phenomenon, a mechanism called an interstitialcy migration was suggested by Kinchin and Pease.\textsuperscript{7} They suggested that a displaced atom in its final stage of motion (that is, when its energy is too low to produce additional displacements) will induce the resulting interstitial atom to travel large distances by a replacement process. Instead of coming to rest and becoming an interstitial atom, the displaced atom will fall into a lattice site and push the atom which occupied that site into the adjacent interstitial location. This latter atom, in turn, would push its neighbor into an interstitial location while it occupied the lattice site. This process would require little energy, and the motion of the interstitial atom would finally cease as a result of frictional losses. There has been some objection to this proposed process on the basis that considerable energy must necessarily be lost unless the atoms strike each other almost head on. Utilization of the concept that the interstitial atom exists as a crowdion would remove this objection, since this defect can only move in specific lattice directions.

Lomer and Cottrell\textsuperscript{8} have postulated that strains set up by an interstitial atom will result in a relaxation, so that the interstitial defect will exist as a crowdion. In this defect it is assumed that the lattice strains, instead of being spherically distributed, are linearly distributed about a row of atoms. This defect is postulated to be in the [110] direction about eight atomic distances in length, and its structure is constrained to move in the [110] direction. Unfortunately, there has been little experimental evidence to support this postulate that the interstitialcy migrates, although Barnes and Makin\textsuperscript{22} have pointed out that this process appears to be the only one which can explain the radiation annealing observed by Cooper and co-workers.\textsuperscript{18} The results of recent experiments at Oak Ridge suggest that defects migrate a long distance from the site of an initial neutron hit. Two separate experiments should be discussed.

Consider first the data obtained on Cu\textsubscript{3}Au. In the initial survey experiments made in hole No. 12, two samples of Cu\textsubscript{3}Au were included which had different thermal histories. One of these samples had a residual resistivity (that is, the resistivity at 15°K) of 4.7212 µohm-cm, while that of the other was 2.5151 µohm-cm. Thus, there was a factor-of-two difference in the resistivity. The results of this run can be seen in Fig. 44. It was quite surprising to note that the electrical-resistivity change

\textsuperscript{21}S. Siegel, Phys. Rev. 75, 1823 (1949).

\textsuperscript{22}R. S. Barnes and M. J. Makin, On the Mechanism of Irradiation Annealing, AERE M/R 1626 (Feb. 1955).
Fig. 44. Effect of Neutron Bombardment on the Resistivity of Cu$_2$Au of Different Degrees of Order. It can be seen that the change in resistivity is unaffected by the initial resistivity. The last point of run 2 in both samples is uncorrected for the large temperature change.

was the same in both samples. There can be little doubt that the change in electrical resistivity is predominantly the result of disordering, for the rate is some ten times greater than that of copper and is in agreement with the disordering rate found in other experiments where the disordering reaction was uniquely shown. In order to check this surprising result, which was at first attributed to some unknown experimental blunder, two additional samples of different order were bombarded in the hole No. 12 cryostat with similar results. (These results are also shown in Fig. 44). It thus seems safe to conclude that the same number of gold-copper pairs is broken in each sample. Another way of expressing this would be to say that the volume of the alloy affected by each neutron hit is determined by the order present. Consider the details of the process for the sample with a resistivity of 1.3 $\mu$ohm-cm (sample A) and for the sample with resistivity of 4.7 $\mu$ohm-cm (sample B). Since the latter sample has a higher percentage disorder, it would be expected that the neutron damage would be less effective in producing further disorder. However, according to Fig. 44, the change in resistivity in both samples is about 0.04 $\mu$ohm-cm. Since the residual resistivity of disordered Cu$_2$Au is about 9 $\mu$ohm-cm, it may be deduced that, in sample A, $3 \times 10^{21}$ atoms are affected per mole. For a bombardment of $5 \times 10^{17}$ neutrons, the number of primary knock-ons will be about $2 \times 10^{18}$, and it may be concluded that for sample A the disordered region is $1.5 \times 10^3$ atoms per neutron hit and for sample B the region is $2.7 \times 10^3$ atoms. The number of disordered atoms per displacement will depend on the number of Frenkel pairs per displacement. If the theoretical number is considered, then about 20 atoms are affected per neutron hit for sample A and roughly twice this, or about 40 atoms per neutron hit, are affected for sample B. An upward revision in these numbers would, of course, be required if the number of displacements per hit were changed. The important consequence that appears is that the disordering process seems to determine the number of atoms affected per neutron hit. Since the disordering energy is relatively small, being of the order of 0.05 eV, a low-energy mechanism should be looked for in order to explain this phenomenon. The mechanism of Kinchin and Pease would seem to be able to explain these data, since the range of the interstitialcy would be determined by the degree of order, as a result of either the increased frictional forces or ordering energy.

Consider now the elastic constant and damping data that have recently been obtained by Thompson and co-workers in the hole No. 12 cryostat. (Thompson and Holmes studied the effect of irradiation on the elastic constants and on the logarithmic decrement in copper single crystals at room temperature in the Graphite Reactor, and they found that their results were explainable on the basis that dislocations are pinned by radiation-induced defects.) A sample, which had been bombarded numerous times at room temperature so that an estimate of the number of dislocations could be made, was given an appropriate heat treatment in order to remove all the effects of the previous bombardments. It was then rebombarded at an ambient temperature of 22$^\circ$K in the hole No. 12 cryostat. It may safely be assumed that there is no defect mobility at this temperature; yet a change, both in the damping and in the elastic constants, well beyond experimental error, was observed. This change proceeded at a rate several orders of magnitude smaller than at room temperature; however, in order to explain the results, it was necessary to assume that each neutron hit must have an

24 D. O. Thompson and D. K. Holmes (to be published).
effective radius of 150 atomic diameters. It is
difficult to imagine a neutron hit producing a
displacement spike of such magnitude that it
would affect a region bounded by a sphere of such
large radius. Not only do the theoretical con-
siderations reject such a picture, but, with such a
volume affected, radiation annealing would be ap-
parent at fluxes much lower than the $5 \times 10^{17}$
neutrons/cm$^2$. Figure 37 clearly shows that no
radiation annealing occurs at this flux. The
interstitial-crowdon mechanism proposed here
would, however, satisfactorily explain the data;
moreover, the interstitial could move 150 atomic
diameters by the interstitialcy process in order to
pin the dislocation. There are, thus, three pieces
of experimental data which would tend to support
the interstitial-crowdon mechanism: (1) the
radiation annealing data of Cooper et al.,$^{18}$ as
analyzed by Barnes and Makin,$^{22}$ (2) the rate
of disordering of Cu$_2$Au in the hole No. 12
cryostat, and, finally, (3) the data of Thompson and
coworkers$^{23}$ on the elastic constant and the
damping of copper single crystals. While these
data should not be construed as overwhelming evi-
dence in support of the interstitial-crowdon
mechanism, it certainly is reasonable to assume
that this mechanism may play a role in radiation
effects. Thus, it would seem that, following bom-
bardment of a pure metal at low temperature, the
interstitial atoms would exist as crowdions and
lie as far as 150 atomic diameters from the source
of the primary displacement. The vacant lattice
sites will remain clustered in the vicinity of the
initial neutron hit, probably within a volume given
by a sphere with a radius of 10 atomic distances.
There may be some damage remaining also as
frozen-in debris from the displacement spike.
With this picture in mind, the annealing kinetics
of low-temperature-irradiated metals will be examined
in the following paragraphs.

Annealing Process I

Process I is the annealing associated with the
motion of defects commencing in the vicinity of
30$^\circ$K. Based on a temperature of 40$^\circ$K, relatively
crude estimates of the activation energy of the
process yield a value of about 0.1 ev, if it is as-
sumed that a unique process occurs and that the
atomic frequency factor is $10^{13}$ sec$^{-1}$. This
hypothetical activation energy is well within the
range of activation energies calculated by Hunt-
gton$^{25}$ for the motion of an interstitial atom. It is
then natural to postulate that process I is the
direct result of the motion and the annihilation of
interstitial atoms; and one school of thought, led
by Seitz and Koehler, supports such a scheme. In
the past six months sufficient data have been
obtained to raise some question as to the feasi-
bility of this scheme. Consider the experiments
which were performed at Oak Ridge for the purpose
of measuring the stored-energy associated with
this process. Samples of high-purity copper crys-
tals were bombarded at 22$^\circ$K in the hole No. 12
cryostat for 160 hr ($4 \times 10^{17}$ nvt). The sample
was then thermally isolated from the cryostat,
and the gamma rays in the reactor heated the
sample. Since the heating is homogeneous, the
slope of the time-temperature curve will be pro-
portional to the specific heat as shown by the
data of Giauque and Meads.$^{26}$ Two such warmups
were determined successively in the range from
15 to 60$^\circ$K. The integrated difference between the
slopes of the two warmup curves is then a measure
of the stored energy. The results are indicated in
Fig. 45. The number of interstitials can be
estimated as $1 \times 10^{19}$ from the resistivity change
of about $2 \times 10^{-9}$ $\mu$ohm-cm and Blatt's scattering
cross section of 1.4 $\mu$ohm-cm/at. %. If all the
interstitials were annihilated at vacancies or dis-
locations (about 5 ev would be liberated per
annihilation), a total energy of about 2.5 cal/mole
would be liberated. The experimental results show
that $<0.1$ cal/mole is liberated. These results
mean either that there are considerably fewer de-
fects than are suggested by the resistivity data or
that this process is not the result of the migration
and annihilation of interstitial atoms. Similar
measurements of the stored energy associated
with this process have likewise been made at
Oak Ridge for high-purity-aluminum single crys-
tals. A very low energy-to-resistivity ratio was
also found for this metal, as can be seen from
Fig. 46.

Consider now the details of the annealing kinet-
ics which were recently studied at Oak Ridge.
Originally it was planned to study isothermal an-
nealing at a minimum of three temperatures so that

an activation energy could be measured. From the results of the first isothermal anneal for aluminum at 35.5°K (Fig. 47), it was apparent that this was not a singly activated process with a low order of reaction; and, thus, the original plan was not carried out. It did seem possible, however, that two processes were occurring: one accounting for the decrease in resistivity in the first pulse, and a second accounting for the tailing-off of the resistivity over longer times. Consequently, the temperature was raised and a second isothermal anneal was made at 42.8°K; and it can be seen that a similar curve resulted at this higher temperature. It thus became apparent that a single activated process did not occur in aluminum, but rather that a spectrum of activation energies was involved. The same conclusion is apparent in the case of copper, cobalt, and nickel. The results are seen in Figs. 48, 49, and 50. In

Fig. 45. The Energy Release Associated with Process I Annealing in a Copper Single-Crystal Sample Which Was Bombarded at 21.7°K for an Integrated Neutron Flux of $4 \times 10^{17} \text{nvt}$. The solid line is the specific heat of copper as given by Giauque and Meads (see ref 26). The energy release in the temperature range of 30–50°K does not exceed 0.1 cal/mole.

Fig. 46. The Energy Release Associated with Process I Annealing in an Aluminum Single Crystal. The sample was bombarded at 19.2°K for an integrated neutron flux of $4 \times 10^{17} \text{nvt}$. The solid line is the specific heat of aluminum as given by Giauque and Meads (see ref 26). The energy release in the temperature range of 30–50°K does not exceed 0.1 cal/mole.

Fig. 47. Isothermal Annealing of 99.998% Aluminum Single Crystals at 35.5°K Following a Bombardment of $4 \times 10^{17} \text{nvt}$ at 18°K. The annealing was done by a pulse technique with all measurements made at a reference temperature of 14°K. Approximately 15 sec was required to bring the sample from 14°K to equilibrium at 35.5°K. Following the isothermal anneal at 35.5°K, the sample was isothermally annealed at 42.8°K and 63.5°K. The ordinate is the ratio of radiation-induced resistivity ($\Delta\rho_p$) remaining after temperature $T$ to the radiation-induced resistivity ($\Delta\rho$).
Fig. 48. Isothermal Annealing of 99.999% Copper Single Crystals Following a Bombardment of $4 \times 10^{17}$ nvt at 18$^\circ$K. The sample was bombarded and annealed simultaneously and under the same conditions as the aluminum crystal described in Fig. 47.

Fig. 49. Isothermal Annealing of Cobalt Polycrystalline Samples Following a Bombardment of $4 \times 10^{17}$ nvt at 18$^\circ$K. This sample was bombarded and annealed simultaneously and under the same conditions as the aluminum crystal described in Fig. 47.

Fig. 50. Isothermal Annealing of Mond-Process Polycrystalline Nickel Following a Bombardment of $4 \times 10^{17}$ nvt at 18$^\circ$K. This sample was bombarded and annealed simultaneously under the same conditions as the aluminum crystal described in Fig. 47. The case of copper, additional isothermal data were obtained which further resolved the change in resistivity that annealed during the first 3 min. The results can be seen in Fig. 51. It can be seen that significant annealing occurred during the first few seconds of the pulse. Recent work on the annealing kinetics of copper bombarded at 18$^\circ$K in hole No. 12 of the Graphite Reactor indicates that the previous history of the copper does not affect process I annealing. A number of different types of copper specimens—high-purity single crystals, zone-refined copper polycrystals, worked and annealed material, and whisker samples were all bombarded and annealed together. An additional sample was also bombarded at 70$^\circ$C for $10^{20}$ nvt prior to insertion in the cryostat. The annealing curves of all these samples were the same in the range from 30 to 50$^\circ$K. These data are indicative of the small distances of defect migration.

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27 T. H. Blewitt et al. (to be published).
28 The zone-refined copper was furnished by W. G. Pfann at Bell Telephone Laboratories.
29 The copper whiskers were provided by D. R. Tumbull and his group at General Electric Research Laboratory.
Fig. 51. Isothermal Annealing at 36.0ºK of Zone-Refined Copper (see ref 28) After Bombardment at 17.5 ± 1ºK for 8 × 10¹⁷ nvt. The sample was pulse-annealed, with all measurements made at a reference temperature of 14ºK. After the anneal at 36.0ºK, the sample was isothermally annealed at 41.4ºK. The first pulse of both anneals was made in a few seconds.

There does not appear to be a satisfactory explanation for process I. It would be convenient to assign the recovery of a frozen-in, liquid-like region to process I. The continuous spectrum of activation energies, the small number of jumps involved, and the low ratio of energy to resistivity would all be compatible with such a scheme. Yet, it seems hardly possible that process I could be completely explained on the basis of frozen-in debris arising from displacement or thermal spikes, since bombardment with 1.3-Mev electrons introduces defects which apparently anneal in accord with process I.19 It may be that the crowddion concept can account for the spectrum of activation energies in process I. In a scheme utilizing the crowddion,8 it is possible that the interstitial moves, after it has been formed, in accordance with a modified Kinchin and Pease mechanism. For relatively high velocities, the interstitial will move in a random direction and dissipate its energy as a result of frictional forces. After it has slowed to the point where its kinetic energy is an electron volt or so, relaxation occurs and a crowddion forms. The energy to move the crowddion and the rate at which this defect dissipates its energy will be small; consequently, the range of the crowddion will be large. It may be that the crowddions, on being formed, will migrate until they are within a few atom distances of a dislocation, vacancy, or impurity atom where the interacting strain fields will hold them; while a few may be held in deeper traps by coming head on with an impurity atom or other defect. It appears that the freeing of the crowddion from these shallow traps by thermal activation would serve to explain the low-temperature-annealing peak,30 since the crowddions, under these conditions, are free to wander about until they are captured by deeper traps or run into a vacancy or an impurity atom. For bombardments in which the integrated flux is small, such as is encountered in hole No. 12, the ratio of vacancies to impurity atoms is small so that in most cases the defects are trapped by the impurity atoms. If the atom is smaller in size than the matrix atoms, then the resistivity also decreases, since the lattice strains are reduced by the capture of a small atom. On the other hand,

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30Since the crowddion is constrained to moving in a line, raising the temperature will not permit combination of the crowddion and the other defect into a deeper trapping state.
larger atoms repulse the crowion with only a slight, if any, reduction in resistivity. Such a scheme satisfies most of the conditions required by experimental results; namely, the ratio of energy to resistivity change is low and a spectrum of activation energies is provided for. Moreover, this scheme would also explain why process I annealing did not occur in alpha brass (see Fig. 52), since the density of impurities is such that the crowion would, in the vast majority of cases, be trapped by these defects immediately, without the need for intermediate shallow traps. Whether or not this mechanism is the principal factor in process I can only be resolved after further experimental data have been accumulated.

These spectra seem to be the result of a continuum of activation energies, since the resistivity appears to decrease continuously at a constant rate in the range from 60 to 240°K. The results of the neutron irradiation can be seen in Fig. 42. Overhauser 31 found that for deuteron-irradiated copper the process apparently had a range of activation energies from 0.2 ev to 0.7 ev. Recent data taken in the hole No. 12 cryostat show that the rate of annealing depends to some degree on the previous history of the specimen. It would seem from the isothermal-annealing results of Fig. 48 that processes I and II are proceeding simultaneously in the range 35 to 60°K. From the tempering curves of Figs. 53 and 54, it would appear that process II is commonly found in most metals; however, in certain instances there have been reports indicating an absence of process II annealing. Figure 55 shows the annealing spectra of platinum irradiated at temperatures in the neighborhood of 18°K in the hole No. 12 cryostat. It should be noted that process II annealing shows considerable variation, with a negligible amount of recovery in one sample. Similarly at Oak Ridge, the absence of process II annealing in copper crystals bombarded at 120°K has been observed and reported.

**Fig. 52.** Tempering Curve for Alpha Brass with 12.9 at. % Zinc. The sample was bombarded at 17.5 ± 1°K for 8 x 10^17 nvt. The data were obtained by pulse annealing, with each pulse of 3-min duration. The measurements were made at a reference temperature of 14°K.

**Process II**

Limited experimental measurements in the range of temperatures associated with process II have been made on copper samples bombarded with electrons, 20 in the cyclotron, 31 and in the reactor. In most cases the samples were bombarded in the vicinity of 100 to 110°K, and in subsequent annealing studies the temperature was raised to 300°K. The electron, cyclotron, and reactor bombardments all show similar annealing spectra.


**Fig. 53.** Tempering Curve for Iron, Following Bombardment for 4 x 10^17 nvt at 18-20°K. The data were obtained by pulse annealing, with each pulse of 3-min duration. The measurements were made at a reference temperature of 14°K.
In general, with different experimenters, there has been considerable divergence in the fraction of the resistivity recoverable by process II.

There have been several suggestions to explain the mechanism of process II annealing. These include interstitial migration to traps, close-pair annihilation, vacancy and divacancy migration to traps. None of these seem capable of explaining annealing. It may be by the utilization of the concept of the crowdion and suitable traps that the phenomenon of process II can be understood. It is difficult, however, to utilize the crowdion concept as an explanation for both process I and process II. It should be noted that once the crowdion absorbs a small-size impurity atom, it becomes immobile. The only way that a crowdion can cause a reduction of resistance is through its acceptance of an impurity atom or its annihilation by a vacant lattice site. The data of Fig. 52, showing the annealing spectrum of alpha brass, would seem to indicate that the crowdion is operative in process I. It is possible that when process I annealing is absent the crowdions have been effectively trapped by the zinc impurities. At the present time, however, further data are required before the mechanism of process II annealing can be adequately explained.

**Process III**

Process III annealing occurs at temperatures ranging from 240 to 280°K in copper. This process has also been observed in other metals, although some shift in the temperature at which it occurs is apparent. In aluminum, for example, the process takes place between 200 and 240°K, as can be seen in Fig. 56; while in ordered Cu₃Au the annealing which occurs in the temperature range 270 to 370°K (Fig. 57) can be attributed to process III. Several interesting experimental facts associated with this process shall now be considered.

Overhauser measured the activation energy associated with the process by making a series of isothermal anneals on copper samples irradiated in a deuteron beam at 100°K. The results showed that if a unique activation energy is assumed its value is 0.7 ev. The order of the reaction seemed to be about 2.5. Similar results were found by Meechan and Brinkman for copper bombarded by
Fig. 56. The Tempering Curve for 99.996% Aluminum Single Crystals, Following Neutron Bombardment for $4 \times 10^{17}$ nvt at 18–20°C. The sample was bombarded and annealed simultaneously with the iron sample described in Fig. 55.

electrons at 80°C and by the Low-Temperature Metal Physics group for copper bombarded in a reactor at 110°C. In all these cases a unique activation energy was assumed, although at present the experimental evidence is not sufficient to prove this assumption.

It has been observed that reactor bombardment of partially ordered Cu₂Au enhances the rate of ordering. This is illustrated in Fig. 58, which shows the results of bombarding partially ordered Cu₂Au in the ORNL Graphite Reactor at 420°C. It should be noted that the resistivity immediately decreased when the reactor started up. Subsequent measurements were made on partially ordered Cu₂Au which was bombarded at 110°C in the reactor (Fig. 59). If no consideration is given to the slight increase in resistivity which occurs during the bombardment and which is attributed to disorder caused by fast neutrons, then no change in resistivity is observed until the sample reaches 270°C. Attempts were made to measure the activation energy of the process, and it can be seen from Fig. 59 that there apparently is no unique activation energy. It is possible that the apparent lack of a unique activation energy can be explained on the basis of there being no homogeneous distribution of defects.

These two experimental facts indicate that process III can be explained by the migration and subsequent annihilation of vacant lattice sites at crowdions, dislocations, or other defects. The activation energy, if it is unique, is in accord with the computed activation energy for the motion of defects. Furthermore, Kauffman and Koehler have experimentally studied the quenching-in of defects and have some evidence that vacant lattice sites should move with an activation energy of about 0.7 ev. The Cu₂Au data suggest some form of vacancy migration. In fact, Brinkman and co-workers have shown that interstitial migration cannot cause ordering, since only the smaller atom of an alloy will migrate. Tentatively, it can be concluded that the ordering associated with process III is the result of vacancy migration.

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**Fig. 58.** Effect of Neutron Bombardment on the Electrical Resistivity of Partially Ordered Cu₄Au.

The sample was prepared by soaking for 36 hr just below the critical temperature and then quenching in brine. The sample has large-ordered domains; the order within each domain is small, however. The neutron irradiation increases the density of vacancies, which have sufficient mobility at 150°C to cause an ordering reaction which results in the decreased resistivity. (From the data of T. H. Blewitt and R. R. Coltman.)

**Process IV**

Relatively very little experimentation has been done on process IV annealing, which occurs at about 600 to 700°C in copper, despite the fact that in many ways it may be of prime importance in so far as the effects of irradiation on the physical properties are concerned. For example, very large changes in the yield stress of reactor-irradiated copper have been reported, even when the bombardment occurred at relatively high temperatures. This fact is illustrated by Fig. 60, which shows the effect of neutron irradiation at room temperature on the critical shear stress in copper single crystals at various temperatures. For comparison, it is worth noting that the addition of 30% zinc (alpha brass) raises the critical shear stress to only 1.8 kg/mm².

The Low-Temperature Metal Physics Group³⁴ studied the recovery of radiation hardness in copper single crystals. The salient features which resulted from this experimentation are that no recrystallization is associated with the recovery process and that the process has a unique activation energy. Subsequently, Kunz and Holden³⁵ determined that the activation energy that was necessary for zinc crystals to recover irradiation hardness was equal to that for self-diffusion. Moreover, Eggleston³⁶ through a study of the recovery of electrical resistivity, confirmed that an activation of 2.2 ev was required in the process IV annealing in copper.

The fact that the activation energy for recovery is similar to that for self-diffusion seems to indicate that the defects responsible for radiation

hardness are eliminated by the creation and migration of vacant lattice sites. It also indicates that the defect must be immobile. The crowdion with a small-sized impurity absorbed in it would have such properties; and it is feasible that this defect can cause the radiation hardness, since it would effectively act as a barrier to the motion of a dislocation. A vacancy moving into such a defect would effectively result in annihilation of the defect by placing the small-sized impurity on a lattice site. Holmes\textsuperscript{37} has developed a theory which explains the salient experimental facts of radiation hardening by the assumption that barriers to the motion of a dislocation are randomly distributed. The concept of an impurity-pinned crowdion would well fit this theory.

\section*{LOW-TEMPERATURE DEFORMATION OF COPPER SINGLE CRYSTALS}

T. H. Blewitt \hspace{1em} R. R. Coltman \hspace{1em} J. K. Redman

\subsection*{Introduction}

Recently the deformation characteristics of copper single crystals have been studied at temperatures ranging down to 4.2 K.\textsuperscript{38} The initial results of this research were reported at the Conference on Defects in Crystalline Solids held at the University of Bristol, July 1954, Bristol, England, and at the Conference on Work-Hardening in Metals held at the University of Birmingham, July 1954, Birmingham, England. Included in these reports was a description of the onset of a change in the mode of deformation after large strains at liquid-helium temperature. At this time it was considered that there were reasonable grounds for suspecting that this anomalous behavior was the result of the deformation changing from a slip process to that of a twinning process. At the Birmingham Conference the suggestion that deformation twinning was occurring in a face-centered cubic metal was not received enthusiastically. In fact, it was clear that incontestable evidence would have to be presented before such a suggestion would be accepted, even though the process occurred in a temperature region and at a stress which were not previously investigated. The unpopularity of this suggestion apparently arose as a result of numerous instances in the

\textsuperscript{37}D. K. Holmes (to be published).

past where strain markings in face-centered cubic metals were incorrectly labeled as twins and as a result of Cottrell’s proposed mechanism of twinning, which precluded twinning in face-centered cubic metals.

Consequently, it was the purpose of the work described in this paper to more fully investigate the deformation of copper at 4.2°K, with particular regard to the new modes of deformation which occur after large strains.

Experimental Procedure

The copper single crystals were grown from 99.999% pure copper prepared by the American Smelting & Refining Co. They were grown in the shape of tensile bars with round cross sections and with square cross sections and were either 1/8 in. or 1/4 in. on an edge. The exact method of growth has been previously described.

The deformation was carried out in an Instron tensile machine. A simple cryostat, which is illustrated in Fig. 61, was adapted to this machine. When utilized for liquid-helium temperatures, the Dewar flask is filled with helium directly from a Collins liquefier and carried to the machine. The consumption of liquid helium is about one liter per 2-hr run; this includes cooling down the machine.

After a high-temperature anneal, the crystals were loaded in the cryostat and were deformed at 4.2 or 77.3°K, the load being measured by the load cell of the Instron machine and the elongation measured by the cross-head motion. In order to test the accuracy of the cross-head motion the elongation was measured by simultaneously utilizing a traveling microscope and the fiducial marks. The results showed that the elongation, as determined by these two methods, differed by less than 0.01 in. for a 1-in. gage length.

The x-ray verification of twinning was performed by a new technique which is described in detail in the next section of this report entitled “The X-Ray Determination of Double Deformation Twins in Copper.”

Results

General Considerations. — The results presented here will show that mechanical twinning occurs in copper single crystals when they are deformed under certain conditions. It will be shown that temperature, orientation, and extent of deformation are important variables in determining whether mechanical twinning occurs. In order to discuss the data concisely, the general features of the process will be considered first, and the particular idiosyncrasies of various samples will be subsequently discussed. In this section, then, the over-all features of the process will be presented with the understanding that, although the samples discussed fall into the general category of typical samples, there are details of the process which differ from sample to sample.

The Load-Elongation Curves at 4.2°K. — It has been previously noted that at 4.2°K the normal slip process results in a linear stress-strain curve. In passing, it should be pointed out that the load-elongation curves show a similar behavior in the region where normal slip occurs. In this discussion, however, attention will be confined to the region where normal slip no longer occurs. Two types of load-elongation curves have been observed when the sample is deformed at low temperatures. These types, which will be denoted as category A and category B, respectively, are illustrated in Figs. 62 and 63.

The orientation of the crystal determines whether the sample has a load-elongation curve of type A or type B. The initial tensile axes of the specimens are represented in the stereographic net of
Fig. 62. Typical Load-Elongation Curve of a Copper Crystal (Sample No. 163) Deformed at 4.2°K Which Falls in Category A (No Twin).

Fig. 63. Typical Load-Elongation Curve of a Copper Crystal (Sample No. 399A) Deformed at 4.2°K Which Falls in Category B.

Fig. 64. Those samples whose load-elongation curves fall in category A are designated by an open circle, those in category B by a filled circle. It is well known that the tensile axis of the sample will rotate during deformation. A deformation of about 50% will take place by normal slip, and this must be taken into consideration in discussing the data. The cross-hatched region in the spherical triangle denotes those samples whose orientation after 50% elongation will have rotated into a position on the dodecahedral plane (that plane represented in the stereographic net by the line connecting the pole of the [100] plane with the pole of the [111] plane) between the [311] plane and the [111] plane. (This demarcation zone was determined by rotating the specimen axis along the great circle connecting the initial tensile axis and the slip direction until it reached the dodecahedral plane, in accordance with the laws of single slip, after which it was rotated along the line representing the dodecahedral plane towards the pole of the [112] plane), in accordance with the laws of duplex slip. It can be seen from Fig. 64 that only those samples with orientations in the cross-hatched region had a load-elongation curve characterized by category B, while those with tensile axes in the open region had a load-elongation curve of category A.

Consider now the details of the load-elongation curve typical of category A, shown in Fig. 62. Beyond the region of normal slip, it is apparent from the discontinuities in the load-elongation curve that a high-velocity localized extension occurs. This region has been designated as the
discontinuous slip region. It should be noted that the sample apparently continues to work-harden with increasing deformation. A clicking noise was heard, which coincided with each discontinuity in the load-elongation curve. The way in which these discontinuities appear on the strip chart is shown in Fig. 65.

After the sample was in the discontinuous slip region, it was electrolytically polished, and all strain markings were removed; the samples were then slightly extended, and the strain markings examined. The results are shown in the photograph Fig. 66.

All the strain markings in this region could be electrolytically etched off, and x-ray measurements with the spinning technique failed to show evidence for the formation of mechanical twins. After considerable deformation, the sample broke in an abrupt manner, as indicated in the load-elongation curve of Fig. 62. The appearance of the fractured region, which is characteristic of category A, is shown in Fig. 67.

Consider now the load-elongation curve of category B. The load-elongation curve of sample 399A, which is representative of this category, is shown in Fig. 63. There is the usual region of slip in which the stress-strain curve is linear; this is followed by a region of discontinuous slip similar to that found in category A. The beginning of a new region, that of twinning, originates with a sharp release of load. In sample No. 397A, the tensile test was stopped when this occurred. The sample was mounted, polished, and etched. The resulting photomicrograph of the initial strain marking, which is believed to be the initial twin, is shown in Fig. 68. A loud report was heard when this twin formed. After the initial twin formation, the load-elongation curve shows no evidence of work hardening, since the load oscillates slightly with elongation. Periodically the sample was removed from the tensile machine and etched so that progress of the twin growth could be followed. Macroscopic pictures of the sample showing this growth are given in Fig. 69. The numbers

![Graph of load vs. elongation](image)

**Fig. 65.** Discontinuous Slip Region of a Typical Crystal (Sample No. 404) Deformed at 4.2°K.
Fig. 66. The Strain Markings Associated with Discontinuous Slip of a Copper Crystal with a Load Elongation of Category A (Sample No. 404). These markings may be removed by etching. Temperature of deformation, $4.2^\circ$K. 500X. Reduced 32%.

of the photographs correspond to the numbers in the load-elongation curve. It can be seen from Fig. 69 that when the sample has completely twinned work hardening once more occurs. Finally, as in the case of samples in category $A$, the category $B$ sample fractures abruptly; the fracture is, however, different from that of specimens of category $A$ in that the fractured surface seems to be along a plane. Figure 70 shows a typical fracture for samples which have load-elongation curves that fall into category $B$.

The Load-Elongation Curve at $77.3^\circ$K. — Twinning has been observed at $77.3^\circ$K in a limited number of specimens. As in the case of deformation at $4.2^\circ$K, the orientation seems to determine whether or not twinning occurs. It appears, however, that only a limited number of orientations will result in the appearance of twins. Those orientations in which twinning has been observed are represented in the stereographic projection of Fig. 64. The load-elongation curves of samples showing twinning (corresponding to category $B$ at $4.2^\circ$K) are shown in Fig. 71. Figure 72 shows the load elongation for a sample which did not show twinning. It should be noted from the load-elongation curve, apart from the twinning phenomenon, that the plastic flow occurs by a normal slip process in both case $A$ and case $B$, without the
presence of a discontinuous slip region. Moreover, it is interesting to note that there is a slight necking down immediately prior to the twinning; then there is an abrupt decrease in load, and the twinning phenomenon occurs. It has been found that the twinning nucleates in the original necked region. The growth of the twin has been studied as a function of elongation in the same manner as was done for samples deformed at 4.2°K. The results showed a high degree of similarity in the two processes. It can be seen from Fig. 71 that, after the twinning material filled the gage length of the sample, deformation again proceeded by a normal slip process. Some degree of necking occurred, and the sample then fractured in an abrupt fashion. The fractured surface appeared similar to that of samples deformed at 4.2°K. On the other hand, those samples which deformed without twinning fractured with a chisel edge in the normal shear-type manner.

**Determination of the Twinning Elements.** – Cohn gives the following definition of twinning: “Two crystals present together in a single coherent piece of solid are said to be in the twin relation to each other if their lattices are related by symmetry about some crystallographically important axis or plane.” Twinning will thus be proved if the symmetry criterion indicated by Cohn can be shown to exist. This was done by utilizing a special x-ray technique developed at ORNL, which is fully described in the next following section of this report. The usual x-ray techniques could not be used because of the extreme amount of distortion present in the crystal when the twinning
phenomenon occurred. This special technique was utilized in the study of many samples deformed at both liquid-nitrogen and liquid-helium temperatures. The results, which are described below, were obtained from one of these samples and are quite typical of the others studied.

Sample 164 was deformed at liquid-helium temperatures until a large twin formed. Figure 73 is a photograph of this sample after deformation. A section about \( \frac{1}{2} \) in. long, containing approximately equal areas of twinned and parent material, was removed from this sample; and the orientation of each was determined by the special spinning technique. Alternate portions of the sample were covered with lead foil, and, as a consequence, it was possible to deduce that the untwinned parent area was a single crystal, whereas the twinned region consisted of two crystals. The orientation of each of these crystals was studied by this technique; and it was determined that one of the crystals in the twinned region had an identical orientation with the parent crystal, whereas the second crystal had an orientation which bore a symmetry relationship to the parent crystal about
Fig. 69. Twin Growth of Sample No. 399A. The numbers adjacent to the photograph correspond to the numbers on the load-elongation curve (Fig. 63).
Fig. 70. Fractured Surface of Sample No. 399A. 20X. Reduced 45%.

the [111] plane. The results are shown in Fig. 74. It should be remembered that, since the [112] plane makes an angle of 90 deg with the [111] plane, the symmetry could also be referred to the [112] plane. It is significant, however, that the x-ray results can only be interpreted if one of the [111] planes is common to both crystals, thereby establishing that the [111] plane is the twinning plane. It can further be noted from Fig. 74 that, in this particular case, the [111] plane utilized in the primary slip system is in actuality the twinning plane.

Consider now the atomic motions on the [111] plane which will result in twin formation. It is commonly accepted that slip proceeds on the [111] plane in the [110] direction. It is furthermore accepted that the atomic motions are in the [112] and [211] directions, with a resultant net motion in the [110] direction, as is illustrated in the vector diagram of Fig. 75. It can also be seen from Fig. 75 that a net atomic motion in the [112] direction (that is, if only one half of the slip process occurs) will change the stacking, since it will move an atom from a B site to a C site. The stacking will thus change from $ABCA$ to $ABCA$.
Fig. 73. Twin Formation in Sample No. 164 Following Deformation at 4.2°K. A section from this sample containing both twinned and parent regions was utilized for an x-ray analysis. 4X. Reduced 9%.

Fig. 74. Standard Projection of a Face-Centered Cubic Crystal Showing the Rotations of the Principal Places for a Twin Relationship. The experimental determination of the twinned principal planes is indicated by a segment of a circle. The initial tensile axis is denoted by TA and the axis at the onset of twinning by TA'.

Fig. 75. Vector Diagram Indicating the Atomic Motions Resulting in Slip. The voids between the spheres will be the sites for atoms in the plane below and the plane above. These positions are denoted by C and A, respectively. (From Cottrell, Dislocations and Plastic Flow in Crystals, Clarendon Press, Oxford, 1953).
A B C A C A B C A. This is called a stacking fault. If, however, a number of adjacent planes glide over each other in this fashion, the stacking becomes A B C A C B A C B A B C A B C, the region between the vertical lines being a twin. The amount of shear, \( S \), associated with this twinning is constant, with a value of 0.707. The amount of elongation associated with this shear will, of course, depend upon the orientation of the crystal relative to the tensile direction. It is given by the following equation:

\[
\frac{l}{l_0} = \sqrt{1 + 2S \sin x \cos \lambda + S^2 \sin^2 x}
\]

where \( l_0 \) is the initial length, \( l \) is the final length, \( x \) is the angle between the twin plane and the tensile axis, and \( \lambda \) is the angle between the twin directions and the tensile axis.

On utilizing the orientation of sample 164, it is found that \( l/l_0 = 1.27 \). For this particular sample, the areas of both the twinned and parent samples were measured. The strain determined from this measurement was 1.29. Thus, there is some indirect evidence that the twinning direction is the [112] direction, although it would be most difficult to expect any other direction after it had been deduced that twinning occurs on the [111] plane.

At the time that twinning was first suspected, an effort was made to determine the orientation of the twin lamellae by measurement of the macroscopic angles that the lamellae made on the crystal surface, together with the angles between the surfaces. Invariably these results showed that the twin lamellae were some 3 to 5 deg from the [111] plane; since the accuracy of this method is not high, this departure was attributed to experimental error. It is apparent from Fig. 68 that this discrepancy arose from the fact that the macroscopic boundary of the twin is composed of a series of twin lamellae which fail to run through the sample and which make an angle of about 5 deg with the boundary.

In some cases twinning occurred on two conjugate [111] planes. The twin formation in sample 167 is an example of this phenomenon. Figure 76 shows the macroscopic appearance of these twins, and Fig. 77 shows a photomicrograph of the interaction of the conjugate twins. Although several interpretations are possible, in the region shown in the photomicrograph, it would appear that the two twins formed simultaneously and then interacted with each other. Apparently, one twin lamella finds it difficult to penetrate the other. Twinning on conjugate planes was observed generally in those samples in which initial orientation was close to the dodecahedral plane. In the immediately following section of this report, considerable attention is devoted to the x-ray determination of the orientation of the conjugate twins of sample 167.

In certain instances strain markings have been observed which have not been identified. Figure 78 shows an example of some unidentified markings. It is apparent that some change in orientation occurs, since etching will not remove the markings. Because of the irregular shape of the markings, it is not yet certain whether this phenomenon is associated with a particular plane. A photomicrograph of these markings is shown in Fig. 79. An additional group of short secondary markings is also apparent. The fact that secondary markings change direction when they pass through the unidentified markings would suggest that this region has a different orientation from that of the matrix. It may be that these markings are the result of another twinning of unidentified elements.

For metallographic polishing, it was necessary to mount the sample in bakelite; thus the temperature reached 150°C for a few minutes. This was sufficient to result in recrystallization as is evident in Fig. 79. It can thus be deduced that the region is in a high state of strain relative to the matrix. This preferential recrystallization of the twinned crystal on heat treatment appears to be the general rule. An additional photomicrograph showing the twin boundary of sample 164 following a 25-min heat treatment at 150°C is presented in Fig. 80. It will be noted here that in only one case did a recrystallized grain penetrate through the twin boundary. Sample 399, which had completely twinned, was observed to be recrystallized after it was stored for about one year at room temperature. The heaviest density of recrystallized grains was visible near the fractured end. The fractured end itself was a fine-grained surface.

**Discussion**

**Mechanical Twinning.** The results presented in the previous section clearly show that mechanical twinning can occur in copper crystals if the
Fig. 76. Recrystallization in the Twinned Region Following an Anneal at 150°C for 25 min. 100X. Reduced 32.5%.

crystals have a specific orientation and if they are highly deformed at temperatures below 77.3°C. The problem still remains, however, to establish the exact mechanism by which this occurs. It would seem at the present time that to attempt to construct a precise theory to account for the formation and growth of these twins would be highly unprofitable because of the present confused concepts concerning the defect structure of highly worked metals. Nevertheless, there are certain facts available from the results which suggest that certain channels may lead to a satisfactory explanation of the process.

One approach may be the effect of orientation on the ability of a sample to twin. The results of Fig. 64 clearly show that twinning will occur only in those samples which have a tensile axis in the dodecahedral plane (the line connecting the [100] and [111] plane in Fig. 64) whose direction lies between the [311] direction and the [111] direction. Moreover, the [311] direction has a symmetrical position between the [112] direction and the [211] direction. This may be of significance, since a dislocation in a face-centered cubic metal is thought to split into two half dislocations whose Burgers vectors are in the [112] and [211] directions. A stacking fault forms between the two half dislocations. Application of a flow stress results, then, in atomic motion in the [112] direction as a result of the motion of one of the half dislocations. If only this half dislocation moves, then a net motion in the [112] direction results; and a stacking fault, or twin, or one atomic thickness is formed. In normal slip the other half
dislocation also moves, resulting in an atomic motion in the [2\bar{1}1] direction. The net resultant from these two half dislocations will be a slip of one atomic distance in the [1\bar{1}0] direction. The process is not reversible, since the half dislocations can only move in the above sequence in order to produce an elongation. It can be seen that the resolved shear stress in the [1\bar{1}2] direction is greater than that in the [2\bar{1}1] direction for those samples in which the orientation lies to the [1\bar{1}1] side of the [3\bar{1}1] direction; whereas the greatest stress is in the [2\bar{1}1] direction for those samples which do not twin. This suggests that twinning can proceed by the separation of the extended dislocation, that is, by moving the half dislocation of Burger's vector (112) and leaving the [2\bar{1}1] half dislocation fixed. This situation can be arranged by having a barrier to restrict the motion of the [2\bar{1}1] half dislocation, provided there is enough stress present to overcome the stacking-fault energy. Cottrell estimates that a stress one-hundredth of the shear modulus would be required. Experimentally, the approximate twinning stress has been measured to be about 25 kg/mm². Since the shear modulus for copper is about 3000 kg/mm², it can be seen that this stress field is the right order of magnitude to separate the half dislocations. In the case of samples oriented for twinning, the [1\bar{1}2] half dislocation will have sufficient stress to climb the barrier, but the [2\bar{1}1] dislocation will remain behind. On the other hand, unfavorably oriented samples cannot twin, since, from purely geometrical considerations, the [1\bar{1}2] half dislocation must
move before the \([2\bar{1}1]\) dislocation can move. Since the stress along the \([2\bar{1}1]\) direction is greater than that in the \([112]\) direction, this dislocation may then have enough stress acting on it to clear the barrier but will be held up by the \([112]\) half dislocation. As soon as the stress has reached an appropriate level, both half dislocations will move as a unit, with slip rather than twinning occurring.

It may be that the above mechanism is oversimplified. One obvious criticism lies in the fact that the orientation for twinning shifts with temperature. It could thus be argued that the \([311]\) position at 4.2\(^\circ\)K is only a matter of coincidence and that if the temperature became low enough there would be no observable orientation effect. This may be the case; yet it would appear possible, in so far as the effect of temperature on the network of dislocations is concerned, that the energy available at 4.2\(^\circ\)K is negligible. Thus, it would appear that the twinning can occur at liquid-nitrogen temperature as a result of the greater resolved shear stress in the \([112]\) direction.

There is some indication that the barrier height might play the predominant role in the process. In most cases the twin nuclei have formed at the ends of the specimen, where the greatest distortion exists. In addition, it has been found in the several cases investigated that the twinning occurs on the primary slip plane, where the greatest density of dislocations would occur. In the case of sample 414 and sample 169, where the sample deformed extensively in duplex slip, twins were found to form on both planes.

Once the first extended dislocation is completely extended, the force tending to keep the two halves of the dislocations together on the
Fig. 79. Unidentified Strain Markings in Sample No. 167. Deformation temperature, 4.2°K. 10X. Reduced 32%.

adjacent atomic planes will become very small, since the stacking-fault energy will be nearly equal to the twin energy. This will then account for the finite thickness of the twin if each plane is populated with dislocations capable of being extended. It should be noted, however, that the region called the twin is in fact not completely a twinned region but is, rather, interspersed with lamellae of the parent material. For example, even after fracture had occurred in sample 399, the presence of the parent orientation could be detected by x-ray analysis. It is apparent also from the photomicrographs that lamellae of untwinned material are present. It is presumably the presence of these lamellae which prevents large amounts of slip in the twinned region, despite the favorable orientation and cross section.

The decrease in the load, following formation of the initial twin nucleus, may arise as a result of the fact that an additional twin-boundary interface is not formed. Thus, the twin lamellae, which do not completely run through the sample and which
account for the 3- to 5-deg angle between the interface and the [111] plane, serve as nuclei for twins, thereby reducing the stress. It should also be noted that the twin forms relatively rapidly, that is, in less than 1 sec per lamella. The thickness of the initial twin is a few millimeters, with the lamellae of subsequent twins being several hundredths of a millimeter.

Discontinuous Slip. — The phenomenon of discontinuous slip is most puzzling, and a satisfactory postulate as to the basic mechanism involved cannot be advanced at present. It is significant, however, that it occurs only at temperatures below 77.3°K.

It may be inferred that this process is not intimately connected with twinning because of the fact that at 77.3°K twinning occurs without the appearance of discontinuous slip. In addition, the phenomenon has also been observed for relatively small strains in single crystals of highly ordered Cu₃Au that were deformed at 4.2°K. It would seem very difficult to imagine twinning in Cu₃Au because of the disordering that would be introduced by the twinning. (No twinning was observed despite the fact that a favorable orientation for twinning was created.)

Fracture. — In the case of the samples which have twinned, it is believed that fracture occurs as a result of literally pulling the atomic planes apart; that is, the theoretical strength has been reached. Consider sample 399. The cross-sectional area of fracture was measured and was utilized to compute, in conjunction with the load, the fracture stress on the fracture plane. The stress on this plane was found to exceed 100 kg/mm². The theoretical strength has been estimated to be one-thirtieth of the shear modulus, which is in accord with the measured value.

Attempts have been made to determine the crystallographic orientation of the fracture, but the results were inconclusive. However, it can be said that the orientation is within 10 deg of the [111] twin plane, which is common to both orientations.

The exact details of the fracture vary somewhat from sample to sample, in that the degree of necking varies. Sample 339 shows less necking than is usually encountered.

Fracture of untwinned samples varies in certain details. Particularly, it is not planar. Flow has been so drastic in the case of these samples that the two halves of the sample cannot be arranged so that the fractured surfaces fit together. Apparently the untwinned lamellae exert an influence and make an apparent planar surface when fracture occurs in the twinned region. The two types of fracture probably result, however, from exceeding the-theoretical strength.

THE X-RAY DETERMINATION OF DOUBLE DEFORMATION TWINS IN COPPER
F. A. Sherrill M. C. Wittels T. H. Blewitt

Twins in single crystals of copper have been produced by tensile extension at low temperatures. The twinning was reported to be related to a single (111) orientation in every specimen that was examined. In subsequent experiments by Blewitt, Colman, and Redman on the deformation processes in copper at 4.2°K, a more complicated twinning process was observed in which two separate and distinct (111) twin orientations were seen in a single specimen.

In order that these observations might be conclusively confirmed, a sample similarly deformed was subjected to x-ray examination. The following discussion is concerned with this x-ray method of analysis and its possible application to twin determinations in highly deformed crystals.

A Laue back-reflection diffraction pattern of the deformed copper crystal is shown in Fig. 81. It is apparent that the x-ray reflections from such a highly distorted lattice are greatly broadened and suffer large losses in peak intensity. Further, it is evident that Laue methods of analysis are impossible to apply to this type of investigation. Any other film method is probably equally inapplicable. These experimental difficulties were overcome by means of a Geiger-counter x-ray technique which utilizes relatively large "single" crystals. This technique makes use of a special device for sample manipulation,

41 To be published.
and the data obtained are employed in a stereographic projection system.

The device, shown in Fig. 82, is an adapter for the Norelco wide-range diffractometer. It furnishes two additional motions to the standard apparatus which, consequently, may be operated (1) manually or automatically, (2) simultaneously or independently, (3) reversibly, and (4) at variable speeds.

Conventional use of the diffractometer for polycrystalline materials requires that the sample-surface normal always bisect the angle $(180 - 2\theta)$, where $\theta$ is the Bragg angle; and this normal is coincident with any given diffracting-plane normal when proper diffraction geometry is achieved. Therefore, if it is desired to observe single-crystal reflections from planes that are not coincident with the sample surface, it becomes necessary to manipulate the sample systematically in order to obtain the correct conditions. This is accomplished most simply by rotating the sample about two independent axes which are 90 deg apart. In the present case, these two axes are the standard diffractometer axis and the specimen-surface normal, as shown in Fig. 83. Rocking angles are measured about the diffractometer axis, and azimuth angles are recorded about the sample-surface normal, as indicated.

With the Geiger counter fixed at a prescribed Bragg angle, the simultaneous rocking and spinning motions of the sample result in a traverse, as shown in Fig. 84. It is seen that the reflecting-plane normal describes a spiral-like path in space and always maintains the angle $R$ with the sample-surface normal. The heavy arrows indicate the simple motion of the sample-surface normal in the x-ray plane. At one position of the traverse, the reflecting-plane normal will coincide with the diffracting-plane normal. At that point, the sample is in the correct position for diffraction; and if $R < \theta$, the Geiger counter will receive the diffracted x rays. Obviously a traverse could be described from the opposite side of the diffracting-plane normal, and the same results could be obtained. In this case, however, when diffracting geometry is achieved, the sample-surface normal would lie on the opposite side of the diffracting-plane normal (Fig. 84), but it would make the angle $R$. This is better illustrated in Fig. 85, which shows the conical paths described by reflecting-plane normals as the sample is spun while the rocking angle is fixed at the only two correct diffracting positions. It is apparent that the azimuth-angle relations are exactly 180 deg apart in these two positions.

Square-cut specimens were employed in this experiment in order to obtain the flat faces necessary to maintain diffracting geometry. Smaller sections of an elongated specimen were placed with a flat face mounted in the steel ring (Fig. 82) that contains the rocking axis in its top surface. A graduated circle on this ring and another at the drive end of the rocking axis (Fig. 83) respectively permit the azimuth and the rocking angle $R$ to be read directly. Correct sample orientation for each reflection is accomplished by first employing an automatic spiral-like search, which furnishes an approximate orientation; and then the manual controls are used to refine this orientation for the exact determination of the
azimuth and rocking angle. The method of analysis finally involves the measurement of these two angles for several reflections and the employment of these data in a stereographic projection. Thus, if twin crystals are present, it is possible to orient the twin portions and determine the crystallographic relation between them.

**Twinning Evidence**

Preliminary examination of the four faces of the square-cut tensile specimen indicated that only two opposing faces would be usable for x-ray measurements. On the two opposite faces which could not be employed, the intersection of two apparent (111) twin systems was macroscopically observed to form a chevron pattern. With regard to the other pair of opposite faces, however, each face exhibited a single, yet different, set of apparent (111) twin bands; and it was these two surfaces that were used for the x-ray measurement.

Prior to tensile extension, the particular specimen which was investigated possessed a single orientation. After deformation, the determination of the presence of multiple crystals was desirable as a preliminary to twin determination. This is easily accomplished in a face-centered cubic structure by searching for crystallographically
equivalent (h00) reflections. Obviously, if the angular relation between these planes is not 90 deg, multiple orientations are present. This simply means that if the rocking-angle sum of any two crystallographically equivalent (h00) reflections is not 90 deg, then the two reflections are related to two crystals of different orientation. Figure 86 is the diffraction trace obtained, using Cu Kα radiation, in the search for {400} reflections as the specimen was automatically rocked at 2 deg/min and spun at 12 rpm. This particular reflection was selected because it has a relatively large Bragg angle (58.48 deg) and because it permitted a larger volume of the lattice to be searched. An intensity “kick” is seen recorded with each spin revolution over the entire peak breadth. Cursory examination reveals that the two reflections observed are not related to a single orientation; thus, the existence of two crystal orientations is established.

The orientation of one of these crystals is plotted stereographically according to the standard positions on the net. The selection of this particular crystal is arbitrary, and subsequently the orientation of the second crystal must be related to this standard orientation. This is
accomplished by employing the rocking angle and azimuth data in a method which will be described in detail in the following paragraphs.

Since conventional stereographic projection is concerned with the plotting of lattice-plane normals, it is well suited to this analysis. (Mathewson gives an excellent description of this stereographic technique.\footnote{For an excellent description of stereographic technique see C. H. Mathewson, \textit{Trans. Am. Inst. Mining Met. Engrs.} 78, 7 (1928), and A. B. Greninger, \textit{Trans. Am. Inst. Mining Met. Engrs.} 120, 293 (1936).}) As previously described, the rocking angles and azimuths are carefully determined for all desired reflections by manually manipulating the adapter. These data are shown in Table 7 for six reflections observed from side No. 1 of the sample. The initial step in the stereographic projection technique is the proper placement of the sample-surface normal, since this normal is used as a base from which all other measurements are plotted. The correct orientation of the sample-surface normal on the standard stereographic net is illustrated in Fig. 87. From Table 7, the observed rocking angles and azimuths for reflections Nos. 1 and 3 are taken and plotted as follows. A trace of all possible surface normals making an angle of 32 deg from [001] is drawn. Similarly, a trace of all possible surface normals making an angle of 24.5 deg from [111] is drawn. The projection trace of these two small circles intersects at two points, one of which is the proper position of the sample-surface normal.

This unique position is \(C\), since the azimuth-angle difference (measured clockwise) between \{400\} and \{222\} (as observed on the adapter) is 161 deg.

The orientation of the surface normal of side No. 1 has been established at \(C\), and the poles from reflections Nos. 1 and 3 have also been placed on the standard stereographic positions. These reflections are designated as being related to orientation A (Table 7). With C as a base point, the remaining data can be plotted by

\begin{table}[h]
\centering
\caption{X-ray Diffraction Data for Side No. 1 of a Copper Crystal, Showing Presence of (111) Twins}
\begin{tabular}{llllll}
\hline
Indices & Reflection No. & Rocking Angle & Observed & Normalized Azimuth & Orientation  \\
& & & (deg) & (deg) & \\
\hline
\{400\} & 1 & 32 & 0 & 284 & 0 & 0 & A \\
& 2 & 44 & 40 & 202 & 278 & 273 & (111) twin \\
\{222\} & 3 & 24\frac{1}{2} & 24\frac{1}{2} & 85 & 161 & 153 & A \\
\{220\} & 4 & 22\frac{1}{2} & 25\frac{1}{2} & 167 & 243 & 251 & A \\
& 5 & 13\frac{1}{2} & 13\frac{1}{2} & 312 & 28 & 20 & (111) twin \\
\{420\} & 6 & 17 & 16 & 227 & 303 & 303 & A and (111) twin \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig87.png}
\caption{Stereographic Placement of Sample Surface Normal.}
\end{figure}
describing arcs with radii equal to the rocking angles such that the corresponding azimuths are intersected for each reflection. The intersection of these arcs determines the position of the poles in relation to all the observed planes with respect to the surface normal of side No. 1 at C. As shown in Fig. 88, the cube axes of a (111) twin relationship on side No. 1 resulted. The calculated and observed rocking angle and azimuth data which confirm this result are shown in Table 7.

At this point, it should be mentioned that the azimuth angles as read from the adapter are related to some arbitrary zero point, since the sample was placed in the spinner ring with no a priori knowledge of its crystallographic orientation. In view of this fact, a more conventional practice was adopted by setting the great-circle trace between [001] and the sample-surface normal as the direction of zero azimuth. All other measured azimuths are normalized with respect to this position.

The sample was then inverted, and a similar set of data was taken from side No. 2 of the specimen. These data are shown in Table 8. Since it was desirable to relate these data to the orientation of side No. 1, it was necessary to invert the projection so that all orientations could be observed in the same projection. From a naïve

![Fig. 88. Stereographic Projection of Double-Twin Determination.](image)

**TABLE 8. X-RAY DIFFRACTION DATA FOR SIDE NO. 2 OF A COPPER CRYSTAL, SHOWING PRESENCE OF CONJUGATE (111) TWINNING**

<table>
<thead>
<tr>
<th>Indices</th>
<th>Reflection No.</th>
<th>Rocking Angle (deg)</th>
<th>Observed Azimuth (deg)</th>
<th>Normalized Azimuth (deg)</th>
<th>Normalized Azimuth Projected (deg)</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Observed</td>
<td>Calculated</td>
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<td></td>
</tr>
<tr>
<td>[400]</td>
<td>1</td>
<td>32</td>
<td>0</td>
<td>232</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>18</td>
<td>17</td>
<td>67</td>
<td>195</td>
<td>165</td>
</tr>
<tr>
<td>[222]</td>
<td>3</td>
<td>29</td>
<td>29</td>
<td>95</td>
<td>223</td>
<td>137</td>
</tr>
<tr>
<td>[220]</td>
<td>4</td>
<td>18</td>
<td>17</td>
<td>355</td>
<td>123</td>
<td>237</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>27</td>
<td>28</td>
<td>268</td>
<td>36</td>
<td>324</td>
</tr>
<tr>
<td>[420]</td>
<td>6</td>
<td>9$rac{1}{2}$</td>
<td>10</td>
<td>286</td>
<td>58</td>
<td>302</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>35$rac{1}{2}$</td>
<td>34$rac{1}{2}$</td>
<td>19</td>
<td>147</td>
<td>213</td>
</tr>
</tbody>
</table>
point of view, it can be assumed that all orientations in the specimen are being viewed from one side alone, as if the sample were transparent. A new surface normal was thus determined at B (Fig. 88), which was slightly displaced from C. This displacement is due to the deformation process which altered the original parallelism of the tensile-specimen surfaces.

Reflections Nos. 1, 3, 4, 6, and 7 (Table 8) could be projected to the standard stereographic positions (Fig. 88) as before. It is obvious that the orientation determined from these reflections permeates the entire tensile specimen and coincides with the standard orientation, A, determined from side No. 1. The calculated and observed data for a second (111) twin relationship are tabulated in Table 8, and the cube axes for this second twin are designated in Fig. 88.

The tensile extension of a copper single crystal at 4.2°CK resulted in the formation of two separate (111) twin relationships which have been designated as double twinning. An original or parent orientation was found to permeate the entire tensile specimen, and two separate (111) twin orientations were related to this original orientation. The twinning relationships were unambiguously determined by an x-ray technique which permitted the analysis of a highly deformed lattice. This technique combined Geiger-counter measurements and geometrical data which were obtained through the use of a special sample-manipulating device. By employment of the geometrical data obtained from two opposite faces of a square-cut specimen, the double-twining phenomenon in a copper single crystal was confirmed.

IN-PILE MEASUREMENTS AT LOW TEMPERATURE OF YOUNG'S MODULUS AND INTERNAL FRICTION

D. O. Thompson T. H. Blewitt D. K. Holmes

Measurements of Young’s modulus and of internal friction of a copper single crystal were made in the course of a week during which the specimen was held at about 20°CK and irradiated with neutrons. The cryostat installed in hole 12 of the Graphite Reactor was used, and the fast-neutron flux was about \( 7 \times 10^{11} \text{ cm}^{-2} \). The modulus and internal-friction measurement techniques were the same as reported previously. Incidentally, it is interesting to note that the miniature f-m radio transmitter employed in the measurements operated continuously at the temperature specified above with no apparent loss in efficiency.

While the data obtained in these bombardments are regarded as rather tentative, they are considered of sufficient interest to warrant reporting at the present time. In Fig. 89 are shown the increase in resonant frequency and the accompanying decrease in internal friction which occur in the crystal as a result of increasing bombardment time. The resonant frequency and the Young’s modulus, \( E \), are related by the equation

\[
 f = \frac{1}{2l} \sqrt{\frac{E}{\rho}},
\]

where \( f \) is the resonant frequency, \( l \) is the sample length, and \( \rho \) is the density. These results are similar to those which have been obtained with


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Fig. 89. Resonant Frequency and Logarithmic Decrement of Copper Single Crystal at 20°CK vs Reactor Irradiation Time.
specimens at room temperature which were bombarded for shorter lengths of time, and they can similarly be interpreted according to the dislocation pinning model. The last two points on each of the two curves will be discussed later.

After about 3300 kw/hr (2 x 10^{15} a/nl) of bombardment time, the reactor was turned off, and the crystal was allowed to warm up. In Fig. 90 the measured resonant frequencies are plotted against temperature; these data indicate that "annealing" is occurring. Evidently there is a process in effect which is increasing the resonant frequency and offsetting the normal temperature decrease between 35 and 40°K. Upon recoiling the specimen to 21°K, the resonant frequency was considerably higher than it was at the end of the bombardment. The second warmup again shows a knee which commences in approximately the same region and continues out to about 55°K, at which point the normal warmup curve seems to resume. Upon recoiling the specimen again to 21°K, the highest value of resonant frequency and lowest value of internal friction were reached. The values of resonant frequency and internal friction after these two warmup runs are shown in relation to the bombardment curves in Fig. 89. After collecting the data for the last warmup curves, the reactor was again turned on, and the crystal was bombarded for a week at approximately 20°K. Measurements of both the modulus and the internal friction were made throughout this bombardment. No significant changes in either the resonant frequency or logarithmic decrement were observed during this time. Thus, it can be concluded that the fractional change in the modulus during this irradiation was less than the fractional change in the crystal length as a result of irradiation. Although no direct measurements of changes in length and density have been made for copper at this temperature, it can be concluded, with some degree of certainty, from room-temperature data that the fractional change in length is less than 10^{-4}. Consequently, the limiting factor in the modulus determinations is the precision of the frequency measurements, which is about 10^{-4} in the present experiments. Therefore, it can be said that the fractional change in the modulus of a sample after bombardment for one week at 20°K was less than about 10^{-4}.

It is interesting to note that a warmup after one week of bombardment gave no indication of a knee, as indicated in Fig. 90 for the first two warmups. Thus, it seems certain that the "annealing" process mentioned above (in so far as effects on the modulus and the internal friction are concerned) was fairly well completed after the second warmup shown in Fig. 90.

The data presented constitute evidence for interstitialcy motion at a temperature of about 20°K, whereby the interstitialcy reaches a dislocation as a trapping site. If dislocation pinning is assumed, which seems quite well established,

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the change in modulus follows the form

\[
\frac{1}{E(t)} = \frac{1}{E_f} + \frac{C}{(1 + \gamma t)^2},
\]

in which \(E(t)\) is the modulus measured as a function of time (or irradiation), \(E_f\) is the final value of the modulus, \(C\) and \(\gamma\) are constants, and \(t\) is the time. At the largest \(\mu t\) value in Fig. 89 prior to "anneal," \(\gamma t = 0.50\). Thus, bombardment to this extent added 50% more pinning points than were present before bombardment. Since the average line-segment length of this crystal was about \(3 \times 10^{-5}\) cm before bombardment, the added number of pinning points is \(0.16 \times 10^5/\text{cm}\). Now, for simplicity, let it be supposed that any dislocation line which passes within a radius \(R\) of a neutron hit is pinned and that those which do not pass within a distance \(R\) are not pinned. The probability that, in a unit volume, one line 1 cm long is pinned is just \(\pi R^2\) (or the circular cross section divided by unit area). Since the total flux up to this point is about \(2 \times 10^{15}\), there have been about \(5 \times 10^{14}\) neutron hits per cubic centimeter. Consequently, it follows that

\[
5\pi R^2 \times 10^{14} = 0.16 \times 10^5,
\]

or \(R\) is about 150 atom spacings.

Since \(R\) is some 15 or more times greater than the value that would be expected for the extent of a region of direct neutron damage (from neutron-energy considerations), and since all defects capable of pinning dislocations are highly immobile at these temperatures, it is clear that another mechanism of damage propagation is necessary in order to interpret the results. At present, the interstitialcy mechanism and its consequences seem to best explain the process.
SPECIAL PROJECTS

THE PRECIPITATION-HARDENING REACTION IN NICKEL-BERYLLIUM
R. H. Kernohan  A. B. Lewis
D. S. Billington

It is of interest to study the precipitation reaction in nickel-beryllium alloys because the ferromagnetic Curie temperature in this material yields a direct determination of the number of beryllium atoms precipitated.

It had previously been found that neutron irradiation at 35°C produced little or no effect on the amount of precipitate in nickel-beryllium.¹ On the other hand, neutron irradiation at 300°C induced more precipitate (in the form of the non-magnetic intermetallic compound nickel-beryllium) than would normally be expected at 300°C.²,³ The results of the irradiation are shown in Table 9.

A number of specimens of this alloy have now been studied in order to learn more about the mechanism of the precipitation process. The experimental technique for measuring the Curie temperature was described in the preceding progress report.³ By means of a simple formula it is possible to determine the atomic per cent of beryllium atoms precipitated. About 20 specimens, 3.5 cm in length and 0.3 cm in diameter, were heat-treated at 1125°C for 2 hr and water-quenched in order to retain all the beryllium in a supersaturated state. The average Curie temperature after this solution heat treatment was 55.2 ± 1°C, corresponding to 14.54 ± 0.05 at. % dissolved beryllium.

One representative sample was chosen to be heat-treated at each temperature. After each heat treatment the resistance, hardness, and Curie temperature were measured. From the latter measurement the amount of dissolved beryllium was calculated, and subtraction from the initial value gave the atomic per cent of beryllium precipitated. The results of the precipitation heat treatments at five different temperatures are shown in Fig. 91. Hardness and electrical-resistivity measurements taken after each increment of heat treatment on three of the specimens are plotted in Figs. 92 and 93, respectively. Hardness measurements showed considerable variation because diamond-point indentations were taken on the circumference of 0.3-cm-dia (⅛-in.) specimens. However, the trend of hardness is clearly apparent. Metallographic studies were also made on the three specimens heat-treated at 400, 450, and 500°C at the conclusion of these age-hardening treatments. The results are indicated in Table 10 and Figs. 94 and 95.

A study of Fig. 91 (keeping the results of hardness, resistance, and metallographic examination in mind) indicates that the precipitation process in nickel-beryllium probably occurs in three stages: (1) nucleation of precipitate particles, (2) particle growth, and (3) growth of precipitate mass (overaging). The arrows pointing

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### TABLE 9. CHANGE IN PROPERTIES OF TWO NICKEL-BERYLLIUM SPECIMENS HEAT TREATED AT 300°C

<table>
<thead>
<tr>
<th>Specimen Condition</th>
<th>Diamond Point Hardness</th>
<th>$\rho$, Electrical Resistivity at 25°C ($\mu$ohm-cm)</th>
<th>Curie Temperature (°C)</th>
<th>Dissolved Beryllium (at. %)</th>
<th>Precipitated Beryllium (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As quenched</td>
<td>160</td>
<td>37.7</td>
<td>55.2</td>
<td>14.58</td>
<td></td>
</tr>
<tr>
<td>annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>435 hr at 300°C</td>
<td>320</td>
<td>33.4</td>
<td>93.0</td>
<td>12.72</td>
<td>1.86</td>
</tr>
<tr>
<td>(control)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiated 435 hr</td>
<td>430</td>
<td>29.6</td>
<td>118.9</td>
<td>11.48</td>
<td>3.10</td>
</tr>
<tr>
<td>at 300°C ($\rho n t = 1.5 \times 10^{18}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 91. Precipitation of Beryllium from a Nickel-Beryllium Alloy.

**TABLE 10. DESCRIPTION OF METALLOGRAPHIC INSPECTION OF NICKEL-BERYLLIUM**

<table>
<thead>
<tr>
<th>Specimen Heat Treatment</th>
<th>Precipitation (at. %)</th>
<th>Relative Volume Visible</th>
<th>Description of Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>915 400</td>
<td>8.9</td>
<td>5</td>
<td>Small areas at grain boundaries</td>
</tr>
<tr>
<td>800 450</td>
<td>10.9</td>
<td>50</td>
<td>Larger areas surrounding grain boundaries</td>
</tr>
<tr>
<td>140 500</td>
<td>11.4</td>
<td>60</td>
<td>Still larger areas</td>
</tr>
</tbody>
</table>
Fig. 92. Hardness of Nickel-Beryllium Alloy as a Function of Time of Heat Treatment.

downward on each line in Fig. 91 may be taken as a time value for the end of stage 1, the nucleation period. It is difficult, of course, to choose an accurate value because the stages undoubtedly overlap one another. It is likewise difficult to decide accurately when stage 2 is completed and stage 3 (overaging) begins, but these have been marked on the curves by arrows pointing upwards.

A summary of the approximate values given on the curves is given in Table 11. In general it appears that the initial nucleation stage is quite rapid and definitely affects the physical properties. The second stage is much slower, with a gradual increase in hardness and decrease in resistivity; and at the end of this stage, about half the available beryllium is precipitated in the form of submicroscopic particles. The third stage begins with the precipitate appearing at the grain boundaries. As this stage continues, more beryllium precipitates, the material softens, and the resistivity continues to decrease.

The data shown in Fig. 91 were also normalized and plotted in order to calculate the activation energy involved in the first two stages. The normalizing equation $q = (P - P_i)/(P_f - P_i)$ was used, where $q$ is the normalized value, $P$ is the amount of precipitate at time $t$, $P_i$ is the amount of precipitate at the beginning of the process, and $P_f$ is the amount at the end of the process. The value of $q$ will then vary between 0 for the beginning of a process and 1 for the end of the process. The curves of normalized precipitation vs log of the time were similar in shape and could be roughly superimposed by moving them along
the abscissa or log-time axis. This was particularly true of the second-stage process. A large part of the difficulty is probably in the selection of a time at each temperature at which the first stage is completed and the second stage begins. Since the normalized \( q \)-value curves are the same shape and if the precipitation process is thermally activated, then an activation energy may be calculated from the equation

\[
t = t_0 e^{E/kT}.
\]

Values of log \( t \) vs 1/\( T \) for the second stage are shown graphically in Fig. 96; the slope of the lines gives the activation energy \( E \). Other values of \( E \) may be found for different \( q \) values representing various stages in the completion of the second stage. The average value is about 2.55 ev or 59 kcal/mole, which is in agreement with previous work on this alloy.\(^4\)

Similar activation-energy calculations on the first stage of the precipitation process were not very successful. However, an approximate value of the activation energy is in the neighborhood of one-half the value of the second stage.

The effect of neutron irradiation on fully annealed nickel-beryllium had produced no effect on the amount of precipitate except when the irradiation was performed at a fairly high temperature. The effect is indicated by point A in Fig. 91, which shows the amount of precipitate found in a specimen irradiated for three weeks at

Fig. 94. Structure of Nickel-Beryllium Alloy After 900 hr at 400°C. 250X.

Fig. 95. Structure of Nickel-Beryllium Alloy After 800 hr at 450°C. 100X.
### TABLE 11. SUMMARY OF PROPERTIES OF NICKEL-BERYLLIUM AT VARYING STAGES OF HEAT TREATMENT

<table>
<thead>
<tr>
<th>Temperature of Heat Treatment (°C)</th>
<th>Precipitate at End of Stage (at. %)</th>
<th>Hardness Value* at End of Stage (DPH)</th>
<th>Resistivity** at End of Stage (μohm-cm)</th>
<th>Time Limits for Stages (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>2.6</td>
<td>[340]</td>
<td>34</td>
<td>0–[0.005]</td>
</tr>
<tr>
<td>450</td>
<td>2.4</td>
<td>330</td>
<td>33.5</td>
<td>0–0.02</td>
</tr>
<tr>
<td>400</td>
<td>1.95</td>
<td>290</td>
<td>34</td>
<td>0.015–0.06</td>
</tr>
<tr>
<td>350</td>
<td>1.35</td>
<td>360</td>
<td>0.05–1</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.25</td>
<td>300</td>
<td>1–10</td>
<td></td>
</tr>
</tbody>
</table>

**Stage 1: Nucleation**

500 7.7 570 25.5 [0.005]–2
450 8.05 560 25 0.02–30
400 8.5 550 24.2 0.06–600
350 1–(20)***
300 10–(1450)***

**Stage 2: Growth**

500 11.4*** 360*** 15*** 2–(140)***
450 10.9*** 380*** 16.5*** 30–(800)***
400 8.9*** 470*** 23.5*** 600–(915)***

*Initial hardness: 160 DPH.
**Initial resistivity: 37.7 μohm-cm.
***Stage not complete; numbers in parentheses indicate hours of final measurement.

300°C. In other words, point A represents the effect of simultaneous heat treatment and irradiation.

An experiment was carried out to discover whether neutron irradiation had any effect on the amount of precipitate formed during subsequent precipitation heat treatment. Four annealed specimens were irradiated at ambient reactor temperature (~35°C) for one month in the ORNL Graphite Reactor (mut ~ 2 × 10¹⁸). These specimens were then heat-treated at 300, 350, 400, and 450°C. The heat treatment was interrupted periodically; the Curie temperature was measured; and the amount of precipitate was calculated. The results are shown in Fig. 97, which is really a reproduction of Fig. 91 with the ordinate units enlarged.

The curves for the irradiated specimen are included for comparison.

Since only one specimen was used as a control and one as an irradiated sample at each heat treatment, quantitative conclusions about the effect of neutron irradiation on the precipitation heat treatment cannot be formed because differences in the curves in Fig. 97 may be due to individual specimen differences. It would appear, however, that irradiation causes an increase in the initial rate of precipitation in the initial stage and possibly a decrease in the amount of precipitate available at the beginning of the second stage. At heat-treatment times longer than are shown in Fig. 97, the curve for the irradiated specimen and the curve for the control specimen are usually quite close together.
squared curves as a function of time at temperature for two samples irradiated with fast neutrons. One sample was irradiated to $10^{19} \text{ neut}_f$ and the other to only $10^{18} \text{ neut}_f$. Although there is considerable spread in the data, due largely to sample inhomogeneities, the effect of the longer irradiation can be seen. Thus, during early heat treatment, growth of the measured precipitates was retarded (however, growth or formation of small precipitates, which cannot be seen, was not necessarily affected), and growth during later treatment was possibly accelerated.

The maximum percentage difference between the slopes for the two samples is roughly the same as that obtained by Jan\textsuperscript{6} on two samples of 70 wt % Al–30 wt % Ag, one of which was cold-worked and the other not, after heat treatment of both samples at 160$^\circ$C. However, his data show that there is no recovery in the cold-worked sample, whereas in the case of the highly irradiated sample (Fig. 98) recovery seems to be complete after 50 hr at 100$^\circ$C. If this difference between the effects of cold work and of radiation is real, then it can be said that the nuclei formed after cold work (to which Jan attributes the retardation effect) are stable, whereas nuclei formed during or after irradiation are not stable.

The last three points in the 3R11B2 plot cannot be fitted to a simple curve that will also include the other points. There is substantial evidence to show that this is due to sample inhomogeneities, the effect of which is not included in the estimated average error shown with each point. The data seem to suggest that the inhomogeneities increase with heat treatment in the irradiated samples.

There are a number of inconsistencies in the data which are not shown here. Two other samples, one standard and one irradiated to $10^{19} \text{ neut}_f$ (though not with identical precipitate size), were heat-treated at 100$^\circ$C for a total of 15 hr, and no appreciable difference in rate of aging was apparent.

Also, in general, the sample irradiated to $10^{19} \text{ neut}_f$ does not show as strong a retardation as do samples\textsuperscript{5} exposed to $5 \times 10^{18} \text{ neut}_f$. This suggests that the effect does not increase monotonically with irradiation.


\textsuperscript{6}J. P. Jan, J. Appl. Phys. 26, 1291, esp 1294 (1955).
Fig. 97. Effect of Heat Treatment on Initial Precipitation Stage of Irradiated and Control Nickel-Beryllium Specimens.

Work more recent than that described here has been concerned with the obtaining of plots of precipitate size vs time at temperature after various irradiations and for various heat-treatment temperatures.

**Small-Angle X-Ray Scattering Technique**

R. E. Jamison

Small-angle x-ray scattering experiments with precipitate alloys, in which the matrix is of higher electron density than the precipitate, had previously been abandoned because of the low intensities involved. However, it has now been realized that a technique described previously can be applied in the study of a few such precipitate alloys.

This technique, in which a Ross filter combination is used for monochromatization, can be applied by allowing the heavy element in the matrix to act as the high-Z filter in the Ross combination. An alloy, of particular interest, which may be studied in this way is nickel-beryllium. For obtaining Cu Kα radiation from a copper-target x-ray tube, the nickel in the alloy

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Fig. 98. The Effect of Neutron Radiation on the Rate of Precipitate Growth in an 80 wt % Al–20 wt % Ag Precipitate Alloy.

One significant fact shown by the calculations is that the intensity of the scattered irradiation in nickel-beryllium will be strongly increased as a result of the increase in electron density of the matrix as precipitation proceeds. Measurement of this increase may be a valuable complement to the slope measurements which themselves indicate precipitate size. The percentage beryllium precipitated (and, thus, the electron-density difference) as a function of heat treatment is known, so that the change in intensity may be an accurate indication of the increase in the number of precipitates.

**SMALL-ANGLE X-RAY SCATTERING FROM NICKEL-BERYLLIUM**

R. E. Jamison | R. H. Kernohan

A few samples of 14.5 at. % Be–Ni foil have been prepared and heat-treated so as to exhibit various stages of precipitation. Preliminary x-ray examinations by the technique described in the previous section show that valuable indications of particle size and particle-size distribution as functions of heat treatment and of heat treatment following irradiation can be obtained.

It is hoped that calculations indicate that the new counting equipment, which has been ordered, and the refinements in the experimental techniques, which are anticipated, will give better results than those qualitative results which have been obtained heretofore.

**PARAMAGNETIC RESONANCE OF IMPURITIES IN MgO SINGLE CRYSTALS**

R. A. Weeks | R. H. Silsbee

Numerous groups of resonance lines have been observed in MgO which are due to the presence of paramagnetic impurities. The spectra observed in single crystals originating from various sources have been described. It has been possible to relate some

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of the lines observed to some of the paramagnetic impurities. In particular, it has been possible to assign the six-line spectrum and associated satellites to Mn$^{++}$. The hyperfine-splitting constant, the satellite structure, and the $g$ value are all in agreement with other observations on the Mn$^{++}$ impurity in MgO.\textsuperscript{10} All specimens that have been examined thus far have had the six-line spectrum and the manganese impurity.\textsuperscript{12} Another line has been tentatively identified as the iron line.\textsuperscript{10} This identification is not certain, since a line with the same $g$ value has been reported as being due to excess oxygen,\textsuperscript{13} that is, to the O$^{-}$ ion.

In some specimens an eight-line hyperfine structure has been observed. This structure has been tentatively identified as V$^{+++}$. The $g$ value and the hyperfine-structure constant, $A$, are in agreement with other observations\textsuperscript{10} on V$^{+++}$ in MgO. One discrepancy in this identification is the lack of satellite structure which would be expected because of the \(\frac{3}{2}\) electronic state.

One other peculiarity observed for MgO is that the fourth line of the Mn$^{++}$ spectrum, counting from the low-field end, has unusual intensity variations when compared with the other five lines.\textsuperscript{14} When the crystal is oriented with its [110] plane perpendicular to the magnetic field, $H$, another line is partially resolved. The width of this line is apparently less than or the same as the manganese hyperfine line and in some orientations has the same line position. No attempt at identification has been made on this line.

In Fig. 99 all the impurity lines discussed above are shown. The line positions given on the figure are the measured values. The measured line position in the case of hyperfine splitting not only includes the spin plus orbital contributions but also contributions from the hyperfine interaction. The relation between frequency and magnetic field is usually written as

$$hy = g\beta H,$$

where $h$ is Planck's constant, $y$ is the r-f frequency, $g$ is the spectroscopic splitting factor, $\beta$ is the Bohr magneton, and $H$ is the magnetic field. This relation is valid in the absence of

\textsuperscript{12}The manganese impurity was identified by activation analysis performed by the Activation Analysis Group of this Laboratory.


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**Fig. 99.** Paramagnetic Resonance of Impurities in an MgO Single Crystal. The impurity spectrum in (a) is due to Mn$^{++}$; the one in (b) has been tentatively identified as V$^{+++}$; and the spectra in (c) have not been identified. One of the lines in (c) is thought to be due to iron. The lines have been separated in this fashion for the purpose of clarity. The crystal was oriented with the [110] direction parallel to the fixed magnetic field. The microwave frequency was 9220 Mc.
nuclear interactions. With such interactions present, as in the case of the Mn$$^{++}$$ ion, the relation becomes\textsuperscript{15}

$$b\gamma = g\beta H + Am + \frac{A^2}{2by} \{ I(I + 1) - m^2 \},$$

where \(A\) is the hyperfine-interaction constant (that is, the experimentally determined separation of the hyperfine lines), \(m\) is the magnetic quantum state (external field being the axis of quantization), and \(I\) is the nuclear quantum state. When the center of the manganese spectral line is calculated from the observed position of the third or fourth line, then the spectroscopic splitting factor becomes \(g = 2.0014 \pm 0.0004\); similarly, for the eight-line spectrum, tentatively associated with \(V^{+++}\), \(g = 1.9800 \pm 0.0004\), which is in agreement with previously reported values.\textsuperscript{10}

PARAMAGNETIC RESONANCES IN IRRADIATED MgO SINGLE CRYSTALS

R. A. Weeks R. H. Silsbee

Several single crystals of MgO have been investigated with fast neutrons, and the resulting effects on the paramagnetic resonance have been observed. Two primary effects are (1) the production of resonance centers whose apparent spectroscopic splitting factor, \(g\), is 2.0022 \pm 0.0004 and (2) a reduction in intensity of the hyperfine lines associated with the Mn$$^{++}$$ impurity. The line shape of the induced centers is somewhat unusual, and the effect on the manganese hyperfine lines was unexpected. The crystal in which these effects are quite strong was given a neutron dosage of \(4 \times 10^{19}\) fast neutrons/cm\(^2\), and the temperature during irradiation was approximately 250°C. The crystal, which was colorless, was dark blue after irradiation. The coloration has not faded appreciably in several months at room temperature.

In Fig. 100 the spectrum in the irradiated crystal is compared with the spectrum in another crystal; the two crystals were cleaved from adjacent positions in the parent crystal. The irradiation-induced line, Fig. 100b, is apparently not a simple one. The satellite structure, which is apparent, is suggestive of the line shape that might be expected from an \(f\) center. It has been suggested\textsuperscript{11} that the resonance spectrum expected from an \(f\) center should consist of a central, very narrow line arising from those centers whose nearest neighbor magnesium atoms are all the isotope Mg\textsuperscript{24}. On either side of the central line there should be additional lines as a result of the hyperfine interaction with the isotope Mg\textsuperscript{25}, whose nuclear spin is \(\frac{5}{2}\). Since this isotope has a natural abundance of 10.05%, most of the remaining centers would have only one Mg\textsuperscript{25} in the nearest neighbor position, the other five being Mg\textsuperscript{24}. The percentage of centers with only Mg\textsuperscript{24} in nearest neighbor positions is 53%; 36% of the centers have only one Mg\textsuperscript{25} atom; and the remaining 11% of the centers should have two or more Mg\textsuperscript{25} atoms in this position. The centers with one Mg\textsuperscript{25} atom in the first shell should have a six-line hyperfine structure whose hyperfine-interaction constant is of the order of 5 gauss. The spectrum from the remaining centers should consist of many lines which cannot be resolved, and whose net effect should be a broad line with the same \(g\) value as the single narrow line.

The second shell of magnesium atoms is 2.3 times further away than the first shell. If the hyperfine interaction is assumed to have a \(1/r^3\) dependence, then the effect of this shell should be an order of magnitude less than the first shell. The effect of the hyperfine interaction of the second shell of magnesium atoms should then be a broadening of the central narrow line.

If the observed line, Fig. 100b, is due to such a center, then the six-line hyperfine structure would be resolved by subtracting the central line from the observed spectrum. If the above assumptions about the central line are correct and if it is assumed that interactions for the paramagnetic impurities are absent [a reasonable assumption in view of (2) above], then to a first approximation the central line may be assumed to have a Lorentzian form\textsuperscript{16,17}

$$\phi(\Delta H) = \frac{A}{1 + \rho^2 \Delta H^2},$$

where \(\phi(\Delta H)\) is the intensity of energy absorbed

\textsuperscript{15} W. D. Hershberger and H. N. Leifer, Phys. Rev. 88, 714 (1952).


\textsuperscript{17} A. M. Portis, Phys. Rev. 91, 1075 (1953).
Fig. 100. Paramagnetic Resonance in MgO Before and After Irradiation. The irradiated crystal received a neutron dosage of $4 \times 10^{19}$ nvt. In (a), a portion of the impurity spectrum is shown before irradiation; the two hyperfine lines are the third and fourth of the manganese spectrum, the weaker lines being satellites. On top of one of the satellites is the line assumed to be due to iron. In (b), the same region of the spectra is shown after irradiation. The measurements were made at 9220 Mc. The crystals were oriented with the $\{100\}$ direction parallel to the magnetic field, $H$. In this crystal no lines were observed which could be attributed to $V^{++}$. 
by the centers at $\Delta H$ gauss away from line center, $A$ is intensity at line center ($\Delta H = 0$), and $p$ is a constant that can be evaluated from the experimental data. Two parameters, taken from the experimental data, are $\phi^*(\Delta H_0)$ and $\Delta H_0$, where $\Delta H_0$ is defined by $\phi^*(\Delta H_0) = 0$, the maximum and minimum points of the curve in Fig. 100. Because of contributions from the remaining centers, it is difficult to determine these two parameters from the data precisely. Thus, several values of $\phi^*(\Delta H_0)$ and $\Delta H_0$ were estimated from the curve in Fig. 100 and were used to calculate the Lorentzian curve. The difference between the observed curve and the Lorentzian curve is shown in Fig. 101. It is evident that the remaining broad central line is stronger than that which would be expected from 10% of the centers with two or more $\text{Mg}^{24}$ and/or $\text{Mg}^{26}$ in the first

**Fig. 101.** The Difference Between the Curve $\phi^*(\Delta H)_\text{obs}$ and the Curve $\phi^*(\Delta H)_\text{calc}$ Plotted for Various Choices of the Parameters $\phi^*(\Delta H_0)$ and $\Delta H_0$. In curve A, $\phi^*(\Delta H_0) = 40$, and $\Delta H_0 = 0.4$ gauss; in curve B, $\phi^*(\Delta H_0) = 39$, and $\Delta H_0 = 0.5$ gauss; in curve C, $\phi^*(\Delta H_0) = 41$, and $\Delta H_0 = 0.4$ gauss. Only one-half of the $\phi^*(\Delta H)$ curve is shown, since there was no evidence of asymmetry.
shell. The spacing of the satellites is not uniform, the separation of the third and fourth lines being almost twice the separation of the others. It seems evident that the simple model postulated above is not adequate to explain the observed line.

No explanation for the decrease in intensity of the impurity lines has been found, other than a very general one which effectively states that the traps in the forbidden band, introduced by the heavy irradiation, drain off the paramagnetic electrons. If this latter explanation is correct, then photoconductivity and optical-bleaching measurements should be helpful in evaluating this effect. Such measurements have not been performed yet. It should also be noted in this connection that the line which has been identified with the iron impurity ($g = 2.003$ for the [100] direction parallel to $H$) is also decreased in intensity. If this were not so, then the irradiation induced line, Fig. 100b, would be asymmetric. It is also possible that the decrease in intensity of the impurity lines is related to the growth of the line discussed above.

PARAMAGNETIC RESONANCE IN IRRADIATED CRYSTALLINE QUARTZ

R. H. Silsbee R. A. Weeks

The paramagnetic resonance spectrum of neutron-damaged crystalline quartz is dominated by a series of lines showing a sixfold structure.\(^\text{18}\)

The resonance is interpreted as arising from a defect characterized by an anisotropic $g$ value and by an electronic spin of $\frac{1}{2}$.

The symmetry of the alpha quartz structure implies that, except for certain lines or planes of symmetry, an arbitrary point in the unit cell is equivalent to five other points and that the crystalline environments of these six points are related by the symmetry operations of the crystal. If a defect is found at one of these points, then it is equally likely to be found at the others; and for a general orientation of the crystal in the resonance experiment, a line arising from each of the six possible positions of the defect can be expected.

The directions and magnitudes of the principal axes of the $g$ tensor may be determined from the variation in the line positions as the crystal is rotated with respect to the applied field. Data were taken at five or six positions by rotating the crystal about each of its three mutually perpendicular axes. By combining the data for the $g$ value in each of these planes, the full $g$ tensors can be constructed for each of the six lines. The $g$ tensors for the different lines must transform into each other under the symmetry operations of the crystal. By applying the appropriate symmetry operations, the various $g$ tensors can be transformed to a common orientation. From a comparison of the directions and magnitudes of the principal axes, the accuracy of the results can be estimated.

The results are given in Table 12. The polar coordinates of the principal axes are $\theta$ and $\phi$, with the crystal $c$ axis as the polar direction and $\phi$ measured from the crystal twofold $x$ axis. The principal values of the $g$ tensor are given as departures from the $g$ measured with the applied field along the $c$ axis ($g_{c \text{ axis}} = 2.0006 \pm 0.0003$), since these relative values are known to greater accuracy than the absolute $g$ value.

<table>
<thead>
<tr>
<th>Axis $\Delta g \times 10^4$</th>
<th>$g_1$ $\pm 0.3$</th>
<th>$g_2$ $\pm 0.3$</th>
<th>$g_3$ $\pm 0.2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$, deg</td>
<td>67.0 $\pm$ 1.5</td>
<td>57.5 $\pm$ 7</td>
<td>48 $\pm$ 11</td>
</tr>
<tr>
<td>$\phi$, deg</td>
<td>12.1 $\pm$ 1.3</td>
<td>93.5 $\pm$ 3.3</td>
<td>127 $\pm$ 12</td>
</tr>
</tbody>
</table>

The appropriate directions for the other five lines may be obtained by setting $\theta' = \theta$ and $\phi' = \phi \pm 120$ deg, and, also, $\theta' = (180 \text{ deg} \pm \theta)$ and $\phi' = -\phi \pm 120$ deg or $-\phi$. The errors quoted are based on the scatter in the results for the six lines, and no attempt has been made to estimate the magnitude of systematic errors.

There is also evidence of hyperfine interaction with the 4.7% abundant Si$^{29}$, which has a spin of $\frac{1}{2}$. The lines are weak and difficult to observe, except with the applied field parallel to the $c$ axis of the crystal. Estimates of the relative intensities are difficult but are reasonably consistent in two different samples. With the applied field along the $c$ axis, two lines at distances of 4.0 and 4.6

gauss from the central line are observed on either side of the central line. Each line has an intensity of approximately 2% of the central line. These intensities suggest that each center is associated with two Si²⁹ nuclei, since the total satellite intensity is of the order of 8%. This is also suggested by the fact that two lines are observed with the c axis orientation.

The observed results are interpreted on the basis of an anisotropic hyperfine interaction, assuming that the defect electron is associated equally with the two neighboring silicones. It is also possible that the two hyperfine components result from the fact that the electron spends a different amount of time on the two silicones. Careful work on the orientation dependence of the lines should distinguish between the two cases.

Assuming the anisotropy to be small, the hyperfine separation will be

\[ E_{\text{hfs}} = g\beta \mu_{\text{Si}} \left\{ \frac{8\pi}{3} |\psi(0)|^2 - \langle \frac{1}{r^3} \rangle + 3 \langle \frac{z^2}{r^5} \rangle \right\} , \]

where \( \langle \cdot \rangle \) represents the expectation value over the electronic wave function, \( z \) is the direction of the applied field, and \( \psi(0) \) is the value of the wave function at the Si²⁹ nucleus. The last two terms give an anisotropy of the form \( (1 - 3 \cos^2 \theta) \) to the hyperfine structure; the first term gives an isotropic splitting. If the vectors between the defect and the two neighboring silicones make different angles with the direction of the applied field, a double line results, as is observed. From the observed splitting, a very rough estimate of these terms can be made, namely,

\[ |\psi(0)|^2 = \sim 0.4 \times 10^{24} \text{ cm}^{-3} , \]

and

\[ \left( \langle \frac{1}{r^3} \rangle - 3 \langle \frac{z^2}{r^5} \rangle \right)_{\text{max}} = \sim 0.3 \times 10^{24} \text{ cm}^{-3} . \]

The value of \(|\psi(0)|^2\) may be compared with an estimate of \(|\psi_{3s}(0)|^2\) for a silicon 3s electron,

\[ |\psi_{3s}(0)|^2 = \sim 40 \times 10^{24} \text{ cm}^{-3} . \]

An estimate of the \( \langle \frac{1}{r^3} \rangle \) for an Si⁴⁺ 3p function gives

\[ \langle \frac{1}{r^3} \rangle = \sim 30 \times 10^{24} \text{ cm}^{-3} . \]

These values suggest that the electron spends only a small fraction of its time on the neighboring silicones, namely, a few per cent or less.

It was hoped that a detailed analysis of the resonance would allow a determination of the nature of the defect. Unfortunately, this has not been possible. The data suggest that the defect is not an oxygen vacancy (analogous to the center in alkali halides), since a much larger hyperfine interaction would be expected. Further, the principal axes of the \( g \) tensor do not reflect the symmetry of the oxygen site. The defect, according to the present interpretation, cannot be at a silicon site (either as an impurity or as a vacancy), since this would give rise to three lines instead of six.

The defect may be an interstitial atom or complex associated in some way with two silicones. Since it is difficult to predict where an interstitial should lie, the orientation of the \( g \) tensor is of no help in substantiating this hypothesis. There are clearly many other possibilities, but these are so arbitrary that no conclusions can be reached.

A detailed analysis of the hyperfine structure might give further information about the defect, but the probability of success did not seem to justify the effort that would be involved.

**NEUTRON-FLUX MEASUREMENTS**

D. Binder J. F. Krause

The program involves the measurement of the fast-neutron flux of reactors (~500 ev) and the

variation of irradiation effects with energy. A boron shield has been fabricated to measure the fast flux by the method of Hurst et al.\textsuperscript{22} The shield will be used in conjunction with Pu\textsuperscript{239}, Np\textsuperscript{237}, and U\textsuperscript{238} foils. In order to compensate for the high fission cross section of Pu\textsuperscript{239} at low energies, it was necessary to insert 1.5 cm of B\textsuperscript{10} in front of the foil. In order to check for leakage, various resonance detectors were irradiated inside the B\textsuperscript{10} shield and inside cadmium. The ratios of the "boron-covered" to "cadmium-covered" activities for cobalt and manganese detectors were 60 and \textasciitilde{} 20, respectively. For no shielding at the resonance energy, a ratio of about two would have been observed.\textsuperscript{23} Therefore, 135- and 340-ev neutrons are strongly absorbed by the shield.

Before the exact effectiveness of gamma rays in displacing atoms was known to the authors, a photoneutron source was used as part of the study to determine the variation of displacements with neutron energy. Depending on the energies involved, neutrons are 100 to 1000 times as effective as gammas. This ratio is sufficiently large for reactor or accelerator irradiations but not for photoneutron sources. The anisotropy-beryllium source used produced detectable effects in n-type germanium with initial concentrations of 10\textsuperscript{13} donors/cm\textsuperscript{3}; but the ratio of gammas to neutrons was of the order of 10\textsuperscript{5}, making the gammas about 100 times as effective as the neutrons.

THE QUENCHING-IN OF LATTICE DEFECTS IN GOLD-CADMIUM

M. S. Wechsler W. J. Sturm

It has previously been reported\textsuperscript{24–27} that quenching from a high temperature produces large increases in the electrical resistivity of the beta-phase gold-cadmium alloy. The additional resistivity induced by the quenching (the "quenched-in resistivity") is larger for higher quench temperatures and obeys the relation

\begin{equation}
\Delta \rho = A e^{-\varepsilon_F/kT},
\end{equation}

where \( T \) is the quench temperature, \( k \) is the Boltzmann constant, \( A \) is a constant independent of temperature, and \( \varepsilon_F \) is the energy of formation of the quenched-in defect. Furthermore, the process by which the quenched-in resistivity anneals out was studied; and a relative relaxation time (or time-scale-adjustment factor), \( \tau(T)/\tau(T_0) \), was determined which is given by the expression

\begin{equation}
\frac{\tau(T)}{\tau(T_0)} = e^{(\varepsilon_M/k)(1/T-1/T_0)},
\end{equation}

where \( \tau(T) \) and \( \tau(T_0) \) are characteristic relaxation times at the annealing temperatures \( T \) and \( T_0 \), respectively, and \( \varepsilon_M \) is the activation energy for motion of the associated defect. Two rod-shaped samples of \( 1/8 \)-in. diameter and containing 49 at. % Cd were investigated.\textsuperscript{27} For sample \( A \), it was found that \( \varepsilon_F = 0.39 \) ev and \( \varepsilon_M = 0.61 \) ev; and for sample \( B \), \( \varepsilon_F = 0.38 \) ev and \( \varepsilon_M = 0.56 \) ev.

These experiments have been continued on a third sample, \( C \), of the same shape and composition as the previous two samples. Figure 102 illustrates the effect of quenching temperature on the quenched-in resistivity, from which it is seen that Eq. 1 is satisfied with a value of \( \varepsilon_F = 0.37 \) ev. For the previous measurements on samples \( A \) and \( B \), the time of hold at the quench temperature, prior to quenching, was kept constant at 1 min, a time sufficiently long to ensure thermal equilibrium at the quench temperature. However, the possibility exists that, particularly for the lower quench temperatures, 1 min. is not long enough for a specimen to attain the equilibrium number of defects at the quench temperature. This matter was investigated by varying the time of hold (up to 10 min) at the quench temperature. Figure 102 shows that even at the lowest quench temperatures, a variation in the time of hold produces no significant effect on the quenched-in resistivity.

The isothermal annealing of the quenched-in resistivity in specimens quenched from 450°C was studied over a somewhat wider range of annealing temperatures than was previously used. The results are shown in Fig. 103, where \( \rho_t \) is

\begin{footnotesize}
\textsuperscript{22}G. S. Hurst et al., Rev. Sci. Instr. 27, 153 (1956).
\textsuperscript{23}D. J. Hughes, Pile Neutron Research, p 138, Addison-Wesley, Cambridge, Mass., 1953.
\textsuperscript{24}M. S. Wechsler, Acta Metallurgica (to be published).
\textsuperscript{25}M. S. Wechsler and T. A. Read, J. Appl. Phys. 27, 194 (1956).
\end{footnotesize}
Fig. 102. Quenched-In Resistivity ($\Delta \rho$) vs Reciprocal Quench Temperature for Gold-Cadmium Sample C. The numbers refer to the time of hold in minutes at the quench temperature prior to quenching.

The initial high resistivity immediately after quenching, and $\rho_f$ is the final resistivity at completion of the annealing process. The relative relaxation time was calculated in a manner discussed previously and is shown plotted in Fig. 104, from which it is seen that Eq. 2 is satisfied with a value $\epsilon_m = 0.58$ ev. For comparison, the results for samples A and B are also shown.

An experimental quantity of some importance in this work is the rate of cooling that the sample experiences during the quenching operation. A rough preliminary measurement, made when these experiments were begun, indicated that the cooling rate was about 200°C/sec for a quench temperature of 450°C. However, such a low cooling rate would appear to be inconsistent with the value observed for the activation energy for motion and with the times for annealing in the range of 50–90°C. If it is assumed that the activation energy for motion is independent of temperature, it is possible to calculate the time that a specimen would need to be held at some lower temperature in order to be equivalent to the time spent during the quenching. In this way, for an activation energy of 0.58 ev and a cooling rate of 200°C/sec, the time spent during the quenching is calculated to be equivalent to more than 120 min at 75°C. If this were indeed the situation, it is clear from Fig. 103 that considerable annealing would take place during the quenching. This would mean that the effective freezing-in temperature would be significantly below the temperature at which the sample is held.
prior to quenching, and this possibility is inconsistent with the fact that the curve plotted in Fig. 102 is linear.

For this reason, it was decided to make a series of measurements of the cooling rate during quenching.\textsuperscript{28} The sample used for this purpose was approximately the same size, shape, and composition as the resistivity samples. Chromel-Alumel thermocouples were attached to the sample in two ways. In the first case, 30-gage Chromel and Alumel wires were spot-welded\textsuperscript{29} individually to the surface close to the mid-point along the length of the sample. The distance between the spot welds was equal approximately to the thickness of the wire. A small amount of Sauereisen cement was applied to the sample in the region of the welds. For this arrangement, the thermocouple voltage was a measure of the voltage at the surface of the sample. In the second case, short lengths of 36-gage Chromel and Alumel wires were spot-welded end to end, and a 16-mil hole was drilled completely through the sample at a point midway along its length, passing across and perpendicular to the axis (see Fig. 105). The thermocouple wires were insulated near the weld with quartz-capillary sleeving, and the thermocouple was pulled through the hole so that the bead at the junction was at a point near the axis. The hole and bead sizes were such that good thermal contact was achieved between the thermocouple bead and the wall of the hole. A small amount of cement was applied at both ends of the hole, and the 36-gage wires were spot-welded to heavier-gage duplex thermocouple wire. In this way, a measure of the temperature on the axis of the sample was obtained.

The sample was quenched in the same manner as the resistivity samples; and the thermocouple voltages were amplified and fed to either a calibrated oscillograph or oscilloscope, as shown in Fig. 105. A variety of voltage sensitivities was used. The results for the cooling rate near the axis are shown in Fig. 106, where it is seen that the temperature decreases from about 435 to 200°C in about 80 msec. The corresponding time for a point on the surface was about 10 msec. Thus the effective cooling rate was found to be of

\textsuperscript{28} T. M. Gayle and O. C. Yants assisted with the instrumentation.
\textsuperscript{29} M. T. Morgan performed the spot welding.
Fig. 105. Schematic Diagram of Apparatus for Measurements of Quenching Rate at a Point Near the Axis of a Gold-Cadmium Sample.

the order of $10^4$ °C/sec, a rate considerably faster than previously supposed. From the data shown in Fig. 106, for a point on the axis, the time spent during the quenching is calculated to be equivalent to about 11 min at 75°C. The axis of the sample cools more slowly than the rest of the sample; and, as seen in Fig. 103, little annealing takes place in the first 11 min at 75°C. Therefore, negligible annealing would be expected to take place during the quenching.

A study has also been made of the effects of quenching on the density, determined by hydrostatic weighing, and on linear dimension, as indicated by strain gages. The measurements were made on a cylindrical bar ($\frac{1}{4}$ in. in diameter and 2 in. in length) with a nominal composition of 50 at. % Au–50 at. % Cd. It was found that the density decreases upon quenching. The change in density was found to vary with quench temperature in the same way as the resistivity (Eq. 1). However, for this sample a value of $\epsilon_F = 0.28$ ev was obtained. The annealing behavior was studied by means of strain-gage measurements, which led to a value of $\epsilon_M$ of about 0.5 ev.

For purposes of comparison, the effects of quenching on the resistivity of the same sample were investigated. The energy of formation, $\epsilon_F$, was again determined to be 0.28 ev. The changes in resistivity and density are shown in Fig. 107. The reason for the difference between the value of 0.28 ev for $\epsilon_F$ for this sample (sample J-3) and the values of about 0.38 ev for samples $A$, $B$, and $C$ is not known. Resistivity measurements of the annealing process after quenching were made at temperatures between 60 and 90°C. The results are plotted in Fig. 108, together with similar measurements made with strain gages that were cemented to the same sample. As can be seen, the characteristics of the isothermal-annealing curves are quite similar for the two cases. A plot of the relative relaxation time vs reciprocal annealing temperature (Fig. 109) leads to a value for the activation energy for motion of about 0.5 ev for the two types of measurements.

The effects of the quenching are being interpreted in terms of the quenching-in of lattice vacancies. Rough theoretical estimates have been made of the changes in resistivity and density due to a concentration of lattice vacancies.
Fig. 106. Cooling Curves for a Point Near the Axis of a Gold-Cadmium Sample.
Fig. 107. Reciprocal Quench Temperature vs the Increase in Resistivity and the Decrease in Density Upon Quenching for Gold-Cadmium Sample J-3.

Jongenburger\textsuperscript{32} estimates that the resistivity of pure gold is increased by 1.5 $\mu$ohm-cm for each atomic per cent of vacancies, and the calculations of Tucker and Sampson\textsuperscript{33} for face-centered cubic metals lead to the result\textsuperscript{31} that

$$\frac{d_0}{d} = 1 + 0.4c,$$

where $d_0$ and $d$ are the annealed and quenched densities, respectively, and $c$ is the concentration of vacancies. In the absence of theoretical information that deals specifically with the material under investigation, these theoretical results are used in order to make an order-of-magnitude estimate of the number of vacancies involved in the quenching process. From Fig. 107, it is seen that upon quenching from 450°C the change in resistivity is 1.72 $\mu$ohm-cm and the change in density is 0.0326 g/cc (the annealed density is 13.911 g/cc). From these data and from the theoretical results mentioned above, it is estimated from the resistivity data that 1.1 at. % vacancies are quenched-in and from the density data that 0.6 at. % vacancies are quenched-in.

It is of interest to analyze the kinetics of the annealing process in terms of the annihilation of the excess vacancies frozen into the lattice by the quenching. A model has been devised whereby vacancies diffuse to edge-type dislocations and are there annihilated at jogs in the dislocation lines. In this connection, a series of measurements are in progress in which the annealing is observed at a fixed temperature (75°C) upon


\textsuperscript{33}C. W. Tucker, Jr., and J. B. Sampson, \textit{Acta Met.} 2, 433 (1954).
quenching from various temperatures in the range 250–500°C. In this way, the initial concentration of excess vacancies can be consistently varied. Experiments are also planned to determine the effect of plastic deformation and neutron bombardment on the annealing process after quenching. In this way, it is hoped that more can be learned of the mechanism of defect production and annihilation in crystals.

OPERATION OF DUAL X-RAY TUBES FROM A SINGLE HIGH-VOLTAGE POWER SUPPLY

F. A. Sherrill  M. C. Wittels

Two x-ray-diffraction tubes are operated simultaneously from the single high-voltage power supply of the water-cooled North American Philips unit. This unit does not contain the milliamper stabilizer; and, as a result, modifications necessary for dual operation are easily made. It should be emphasized that the simultaneous operation of the x-ray tubes is conducted under conditions of full-wave rectification and optimum power rating; the tubes are separated about 6 ft on adjoining work tables.

An oil-filled high-voltage switch located on the high-voltage post of the transformer permits the diffraction tubes to be operated independently or simultaneously. The main unit provides the high voltage necessary for efficient operation of the second or remote tube; a 20-ft length of high-voltage cable connects the two units. In the table for the remote unit, an insulated 0- to 5-amp a-c ammeter was inserted in series with the filament of the remote x-ray tube. Similarly, a 2-ohm 100-w rheostat was placed in series with the filament of the main-unit x-ray tube. Employment of this rheostat in conjunction with the a-c ammeter permits the two x-ray-diffraction tubes to be operated simultaneously with any desired number of milliamperes on each tube.

For protective purposes, a contact meter-relay was installed. The voltage for indirect operation of this relay was taken from a 2-ohm 2-w fixed resistor inserted in series with the primary of the filament transformer. In the event that the filament of one of these x-ray tubes burns out this relay disconnects the power and thereby prevents the other x-ray tube filament from receiving an excessive surge of current.
SOLID STATE PROGRESS REPORT

Several hundred hours of continuous and simultaneous operation with molybdenum- and copper-target x-ray tubes have been obtained under optimum power-output conditions. The advantages of dual operation are numerous, especially with regard to film techniques.

X-RAY EXAMINATION OF MISCELLANEOUS IRRADIATED SPECIMENS
G. E. Klein

Molybdenum Wire
Fansteel molybdenum wire 0.001 in. in diameter, tied to a silicon sample before irradiation in the ORNL Graphite Reactor at ambient temperature, was used as a suspension in susceptibility studies of the silicon irradiated with $2 \times 10^{18}$ fast neutrons/cm$^2$. The molybdenum wire was examined by means of a 114.59-mm-dia x-ray powder-diffraction camera.

No change in lattice constants, change in preferred orientation of the sample, or line broadening was noted in the x-ray patterns of the irradiated and unirradiated wire.

Asbestos
A layer of asbestos, to act as a thermal shield, was placed between the outside of the neutron reflector and the inside of the concrete shielding of the ORNL Graphite Reactor at the time of construction. In 1956 some of the layer was dug out, and a sample was examined by x-ray and petrographic-microscope methods. The material had been subjected to gammas amounting to approximately $10^{18}$ r.

The x-ray examination showed a slight change from normal asbestos, such as is characterized by a slight disordering, with a lessening of the degree of x-ray crystallinity and a slight amount of line broadening. The pattern still showed a considerable degree of crystallinity to be present.

The optical examination by G. White of the Metallurgy Division showed the material to be chrysotile, with no changes in optical properties from normal chrysotile.

Since no record was found concerned the exact nature of the original material, all x-ray and optical comparisons can only be made assuming that the material was normal chrysotile initially.

A SPECIMEN ROTATOR FOR THE RADIODIFFRACTOMETER
G. E. Klein

Samples which have been rolled, cold-worked, or pressed frequently exhibit preferred orientation and are difficult, if not impossible, to use for obtaining x-ray diffraction patterns in the normal manner, since the diffracting planes may not be oriented with respect to the x-ray beam so as to be in a reflecting position. If the same samples are rotated, the planes along which the atoms are oriented are brought into reflecting position at least once for each 360 deg of rotation.

A sample rotator, designed by the Engineering Division and constructed in the Research Shops, has become an integral part of the sample holder in the radiodiffractometer. When mounted in the rotator, the sample may be rotated in either direction at approximately 30 rpm, or it may be stopped at any point in its travel. Samples may also be examined in the conventional stationary manner.

THERMAL CONDUCTIVITY OF IRRADIATED NONMETALS AT LOW TEMPERATURES
A. Foner Cohen  L. C. Templeton

Germanium
Measurements of the thermal conductivity of pure germanium single crystals at low temperatures have been continued. In the previous semiannual report, it was shown that after bombardment by fast neutrons annealing effects were in evidence. After a second neutron bombardment, the same specimen was heat-treated; and subsequent measurements, shown in Fig. 110, present evidence of an increase in the thermal conductivity at low temperatures.

Another series of experiments have been completed in which a different germanium single crystal of high purity (specimen E P Ge II) was used, and initially it had a room-temperature electrical resistivity of 40 ohm-cm. The initially unannealed

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Fig. 110. Thermal Conductivity of a Germanium Single Crystal vs Temperature (Specimen Bell Ge II).

crystal was measured (curve 1, Fig. 111). It was then removed from the apparatus, annealed at 400°C, and reinserted. The resulting annealed thermal-conductivity values were higher over the entire range of measurement (curve 2, Fig. 111). Next, the crystal was irradiated with fast neutrons, and the resulting decrease in thermal conduction is shown in curve 3, Fig. 111. It should be noted that measurements were carried out very shortly after the bombardment (see schedule, Fig. 111). The specimen was then annealed at 425°C, and the measurements were made very shortly thereafter. The values of thermal conductivity, over the whole region of measurement, were higher (curve 4, Fig. 111) than those of the annealed unbombarded specimen. The specimen was kept under vacuum in the apparatus; and after approximately seven weeks, another series of measurements was carried out in the region of liquid-helium temperature. At that time the thermal conductivity (curve 5, Fig. 111) had returned approximately to the annealed unirradiated value.
However, according to theoretical predictions, the temperature region below that at which the maximum in the thermal conductivity occurs (for a given sample) should be affected only by the "boundary resistance" or the geometric dimensions of the crystal. This would indicate that in the region below the maximum an explanation for the decrease in thermal conductivity as a result of neutron bombardment cannot be attempted at this time.

It should be mentioned that in the thermal-conductivity experiments of Rosenberg,\(^{36}\) in which \(n\)-type germanium single crystals and \(p\)-type germanium crystals were used, the behavior in the "boundary scattering" region is much the same as is found in our specimens before and after neutron bombardment. That is, the \(p\)-type germanium has a lower conductivity than the \(n\)-type. Since our germanium specimens are initially \(n\)-type and are converted to \(p\)-type upon neutron bombardment, the agreement, noted above, with Rosenberg's experiments is reasonable. In other experiments by Rosenberg, two samples of germanium were used. In one, dislocations were intentionally introduced by bending at 600°C; the other was the control specimen and it was merely heat-treated at 600°C.

The resulting low-temperature thermal-conductivity measurements showed that the cold-worked specimen had a lower conductivity than the control over the whole region of measurement, including the "boundary scattering" region. Whether or not the dislocations themselves are responsible for the phonon scattering in the very low-temperature region is not known at this time.

### Lithium Fluoride

The introduction of extra thermal resistance in the lowest temperature region (boundary-scattering region) by fast neutrons has been examined with crystals other than germanium. Figure 112 shows the curve of the thermal conductivity of an annealed single crystal of lithium fluoride and the curve obtained very shortly after irradiating the same crystal with neutrons. The crystal was entirely covered with a \(\frac{1}{4}\) in. thickness of cadmium during the irradiation. Figure 113 is a plot

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Fig. 112. Thermal Conductivity of a Lithium Fluoride Single Crystal vs Temperature (Specimen LiF I).
Fig. 113. Increase in Thermal Resistivity, Due to Neutron Irradiation, of a Single Crystal of Lithium Fluoride vs Temperature.

showing the increase in thermal resistance as a result of the neutron bombardment; the ordinate $\Delta(1/K)$ is equal to $1/K'' - 1/K'$, where $K''$ is the thermal conductivity of the irradiated annealed specimen, and $K'$ is the thermal conductivity of the same specimen, but unirradiated. The qualitative behavior of the introduced thermal resistance in lithium fluoride as a function of temperature is similar to that found in neutron-bombarded Al$_2$O$_3$, as reported by Berman, and is also similar to that found in our experiments with neutron-bombarded germanium.

Potassium Chloride

On the assumption that very pure starting material is available, potassium chloride would be of interest for use in connection with low-temperature thermal-conductivity studies. With this material, it would be possible to test current theoretical calculations concerning lattice scattering. On the basis of the information thereby obtained, the means of introducing thermal resistance, as caused by various types of defects, may be deduced. Ultimately, these studies may lead to an understanding of the nature of lattice defects. In this connection, some preliminary experiments have been carried out with potassium chloride single crystals. The thermal-conductivity changes ensuing as a result of bombardment by gamma rays and fast neutrons have been investigated.

A single crystal of potassium chloride, designated KCl "J", was provided by R. L. Sproull of Cornell University and was used for the first experiment with fast neutrons. The crystal had two cleaved surfaces and two surfaces ground with sandpaper. It was first measured "as is" in the unannealed state, and curve 1 in Fig. 114 illustrates the thermal-conductivity behavior of the crystal as a function of temperature. After the crystal was annealed for 1 hr at 600°C in vacuum and furnace-cooled, measurement revealed a marked increase in conductivity, as seen by curve 2. The data in the dotted section of the curve showed a large amount of scatter. As a first experiment with fast-neutron bombardment, the crystal was given a short irradiation, and the measurements were made shortly thereafter. The resulting decrease in conductivity is given in curve 3.

From a given initial piece of Harshaw KCl, two single crystals, identified as KCl "C" and KCl "G", were cleaved. Neither crystal was annealed. The thermal conductivity of the KCl "C" crystal was measured and plotted as a function of temperature. The results are shown in Fig. 115. On the same plot are shown three curves obtained with crystal KCl "G" irradiated with Co$^{60}$ gamma rays, as indicated on the figure. It is interesting to note that the successive gamma bombardments caused annealing of the KCl "G" crystal (the annealing of ionized impurities or lattice strains present in the initial crystal are possible explanations). In Fig. 116, $\Delta(1/K)$ is plotted against temperature; $\Delta(1/K) = (1/K' - 1/K'')$, where $K'$ is the

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Fig. 114. Thermal Conductivity of a Potassium Chloride Single Crystal vs Temperature (Specimen KCl "J").
**Fig. 115.** Thermal Conductivity of Potassium Chloride Single Crystals vs Temperature.
thermal conductivity of unirradiated, unannealed KCl "C", and $K''$ is the thermal conductivity of KCl "G" successively irradiated three times with gamma radiation from Co$^{60}$. This figure is included to give an indication of the temperature dependence of the thermal resistance. Further experiments with gamma rays on initially well-annealed single crystals are anticipated.

Measurements of greater precision in the region of 15 to 100K will be undertaken with the crystals in the hope that correlation with theoretical predictions, regarding the nature of defects caused by irradiations of various sorts, can be more fully understood.

Fig. 116. Decrease in Thermal Resistance, Due to Gamma Irradiation, of a Potassium Chloride Single Crystal vs Temperature.