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ANNUAL PROGRESS REPORT
FOR PERIOD ENDING AUGUST 31, 1959

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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For Period Ending August 31, 1959

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OAK RIDGE NATIONAL LABORATORY
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SOLID STATE DIVISION ANNUAL PROGRESS REPORT

SUMMARY

THEORY OF RADIATION DAMAGE

Classical Scattering Theory for Interatomic Collisions

The classical scattering of an energetic, moving lattice atom from a stationary lattice atom is investigated in detail. The study was originally motivated by the need to examine the "hard-core" approximation to the energy transfer distribution. However, the results are of general interest since the method used is limited only by the validity of the interatomic potential assumed. Various general aspects of the scattering are discussed, and particular results for inverse power potentials and "cutoff" potentials are presented. For the case of the screened Coulomb (Bohr) potential, the differential cross section for scattering as calculated on the Oracle is given as a function of the transferred energy for primaries of kinetic energies ranging from a few hundred electron volts to hundreds of kilovolts.

Cross Sections for Atomic Displacements in Solids by Gamma Rays

Cross sections for the displacement of lattice atoms by gamma rays up to 5 Mev have been calculated. In this energy range it is found that the Compton electrons produced by the incident gamma rays are primarily responsible for producing atomic displacements.

The Range of Radiation-Induced Primary Knock-Ons in the Hard-Core Approximation

A theoretical study has been made of the slowing down process for a primary displaced atom in a solid. In particular the range has been calculated, assuming a screened Coulomb potential with the hard-sphere angular distribution after scattering, and compared with experimental values.

Small Amplitude Motions of Dislocation Loops

The small amplitude motion of dislocation loops is investigated in detail, taking into account the whole elastic field interaction between different parts of the loop. An effective line energy is

calculated by a variational procedure and compared with the results of the usually assumed line energy model, which disregards interactions between distant parts of the loop. For large effective line energies, where screw and edge dislocations are almost energetically equivalent, the results of the line energy model are correct. For small effective line energies, the behavior of the core presumably is decisive. The behavior of additive pinning of one loop is investigated. The interaction between the two subloops decreases the apparent line energy and makes the pinning somewhat less effective. The kinetic energy is calculated, and it is shown that the elastic theory gives dependable values. Furthermore, the kinetic behavior of edge and screw loops does not depend very much on the elastic data. Only elastically isotropic media are treated.

Studies on the Structure of Radiation-Induced Displacement Cascades

The extension and internal correlations in a radiation-induced displacement cascade are investigated in detail. The hard-core approximation is used for an approximate description of interatomic collisions. The numerical data apply to copper. The potential used for this substance is a combination of a screened Coulomb potential and a pure exponential potential. The data for this potential can be matched by comparison with experimental data. Shapes and densities are discussed in detail. For the most interesting primary energies less than 5×10^4 ev the shape is rather spherical, and the density of defects is of the order of 5 at. % in copper. For a material like germanium, the defect densities would be smaller by about one order of magnitude.

Approximate Treatment of Annealing with a Spectrum of Activation Energies and First-Order Kinetics

A special model for annealing of defects in solids is discussed. This model is based on first-order kinetics applied to defects which have a continuous distribution of apparent activation energies. An approximation is found which allows

for convenient analysis of experimental data. The limits of the approximation and possible applications are discussed.

DISLOCATION INTERACTIONS

Effect of Fast Neutron Bombardment at Various Temperatures upon the Young's Modulus and Internal Friction of Copper

Studies have been made of the variations of internal friction and elastic modulus during irradiation of pure copper crystals at a number of temperatures in the range 90 to 300°K. The results are interpreted in terms of pinning of dislocation lines by radiation defects migrating from their points of origin. In terms of the room temperature value the dislocation pinning rate is 2.5×10^{-2} in the range 100 to 140°K and (from previous measurements) of the order of 2.5×10^{-5} at 20°K. On slowly warming the sample after the irradiation, it is found that at 260°K the modulus and decrement begin to move rapidly toward their "saturation" values. Presumably defects "stored" in the sample due to a lack of thermal mobility at the irradiation temperature become mobile at this temperature and move to the dislocation lines.

Dislocation Contribution to the Temperature Dependence of the Internal Friction and Young's Modulus of Copper

Using neutron irradiation as a tool, it has been shown that there are at least two dislocation contributions to the Young's modulus and internal friction of copper at low temperatures. These are the Bordoni relaxation spectrum due to dislocation movement over the Peierls potential and an associated background component which seems to fit with a dislocation bowing model. These are studied in detail.

Elastic Constant-Internal Friction Spectrometer

An apparatus has been developed which makes possible the continuous observation of the Young's modulus and internal friction of a metal sample. These physical properties are measured as a function of other environmental conditions surrounding the sample.

LOW-TEMPERATURE IRRADIATION STUDIES

Annealing Kinetics of Neutron-Irradiated Aluminum and Copper

Activation energies for the annealing of copper and aluminum following reactor bombardment near 4°K have been measured. The values measured appear to be too high to be accounted for by a single annealing process. The absence of annealing peaks in the region from 4 to 30°K seems to preclude the existence of discrete annealing processes in this temperature region. It is suggested that the activation energies measured are not those required to move a defect but rather are those required to release the defect from a trap and then move it.

Irradiation Annealing Studies of Various Metals

Isochronal annealing studies of Cu, Ag, Au, Pt, and Zn have been made after neutron bombardment of these materials at 4°K. Except for a shift in temperature, the annealing characteristics found in some of these materials is similar to that found in copper. The annealing of gold is quite anomalous compared to copper and silver in that no large annealing peak is found. Damage rates, calculated from measured changes in residual resistivity on a large number of materials, show wide variations. It has been found that bismuth is damaged at a rate 10^4 that of copper.

The Effect of Annealing in Oxygen on the Residual Resistivity of Copper

It has been confirmed that the residual resistivity of high purity copper can be greatly reduced by annealing in an oxidizing atmosphere. Quantitative data has been obtained showing the time dependence of the decay of resistivity of copper upon annealing at 700°C in 30 μ of air. The resistivity can be restored by annealing in various reducing atmospheres. These results suggest that measurements of residual resistivity may not be reliable for judging the purity of a metal.

Stored Energy of Irradiated Copper

A redetermination of the stored-energy release in reactor-irradiated copper between 30 and 50°K was made under much more favorable conditions

with new refinements of the nuclear-heating calorimetry method. The result confirms earlier figures with a much higher certainty.

Design of a New Low-Temperature In-Pile Facility with a Neutron Converter

The design of a new facility for irradiation-damage experiments at very low temperatures is described. The facility will be placed in Hole 10 of the ORNL Graphite Reactor. In addition to the helium-gas-cooled cryostat, which will operate at about 20°K, it contains a water-cooled neutron-converter tube, which will provide an increased damage rate and allow some studies of the influence of the neutron spectrum on the radiation damage of metals.

Determination of the Gamma Flux and Neutron Flux in the Pool of the ORR

A helium-gas-cooled facility has been installed in the pool of the ORR, which allows samples to be irradiated at about 50°C in an inert atmosphere. Measurements of the gamma heating in this facility, which turned out to be 0.7 w/g, are described. The effective neutron flux (1/E distribution) has been calibrated by measuring the change in electrical resistivity and critical shear stress of copper single crystals and corresponds to a flux of 5×10^{13} neutrons·cm⁻²·sec⁻¹.

The Resistance Minimum and Resistivity of Copper at Low Temperatures

A resistance minimum is found in copper samples after a heat treatment in a reducing atmosphere. Annealing in an oxidizing atmosphere removes the minimum and reduces the resistivity in this temperature range. This phenomenon is reversible, and it is believed that complexes of oxygen and impurity atoms are responsible for this behavior.

ELECTRON MICROSCOPE STUDIES

Fission fragment tracks in thin films of UO₂ have been studied and found to be essentially a surface effect in which material at the surface is displaced as a result of the passage of the fission fragments. Observations on a structure introduced into gold films by fast-neutron irradiation indicate that it is a structural defect resulting from the irradiation, but these observations have not permitted positive identification. An improved replication technique for copper, which is currently in

use on studies of the surface structure of deformed copper, is described.

CHEMICAL PROPERTIES OF METAL SURFACES

The kinetics of the dissolution of copper crystals in aqueous solutions has been investigated. Examination of the surface structure after dissolution indicated that the mechanics of dissolution was complicated and probably not related to crystal imperfections in a simple way. It was shown that, provided certain impurities were present, dislocations in copper were related to oxide nuclei. The technique of detecting dislocations as etch pits was used to study deformation processes in copper crystals. Direct evidence was obtained for dislocation interactions.

DIFFUSION OF DEUTERIUM IN DEUTERON-IRRADIATED COPPER

The diffusion of deuterium in deuteron-irradiated copper is being studied in the temperature range $-50 < T < 50^\circ\text{C}$ by monitoring neutrons from the $D(d,n)\text{He}^3$ reaction. An analysis of the results shows that surface effects are rate-controlling through much of the time of an experiment. For a particular target, irradiated at 18°C, the diffusion coefficient of deuterium is found to be about $(2.60 \pm 0.15) \times 10^{-2}$ (deuteron range)²/sec, or about $(6.92 \pm 0.40) \times 10^{-10}$ cm²/sec. Inclusion of the finite thickness of the diffusion source in the model is found to be unimportant.

ALLOY STUDIES

Experiments are being conducted on the effect of irradiation on atomic rearrangements in binary alloys of several types. These include (1) Cu-Al (15 at. % Al), terminal solid solution; (2) Ni-Be (15 at. % Be), substitutional precipitating alloy; (3) Ni-Cu (28 at. % Cu), an alloy that forms a continuous series of solid solutions; (4) Au-Cd (50 at. %), intermetallic compound; (5) Fe-C (0.008 wt % C), interstitial precipitating alloy.

Additional information has been obtained on the process that causes a decrease in the resistivity of Cu-Al (15 at. % Al) upon neutron irradiation at 40°C. It is found that the decrease in resistivity may also be produced by gamma irradiation at 18°C.

Also, the decrease in resistivity upon neutron irradiation is accompanied by a decrease in specific volume. Furthermore, the neutron irradiation has been carried out at a series of temperatures between 45 and 250°C, which indicates that, although the reaction is speeded up upon raising the irradiation temperature, the magnitude of the effect is diminished. These results are consistent with the notion that the alloy is in a metastable state upon initial cooling from a high temperature and that the irradiation permits the metastability to be eliminated with an attendant decrease in resistivity. However, when quenched alloys are irradiated at -128°C, it is found that, although a portion of the quenched-in resistivity anneals out rapidly, the remainder becomes stabilized. But, if the annealing is done in the reactor at 45°C, all of the quenched-in resistivity is annealed more rapidly than is the case for annealing out of the reactor at the same temperature.

The effect of neutron irradiation on solution-annealed and quenched Ni-Be (15 at. % Be) is shown to be qualitatively similar to the effect on quenched Cu-Al. Also, no re-resolution of the precipitate is found to take place upon irradiation at 35°C of Ni-Be alloys in the aged condition.

Experiments on Ni-Cu (28 at. % Cu) alloys indicate an increase in Curie temperature and a decrease in electrical resistivity upon neutron irradiation at about 20°C. Also, a decrease in Curie temperature is obtained upon quenching from 600 and 700°C. These observations suggest that the equilibrium configuration at lower temperatures involves some amount of segregation of copper and nickel atoms. The irradiation is thought to facilitate the attainment of this equilibrium.

A torsion pendulum has been used to measure the damping capacity of a carburized alpha-iron wire in preparation for a study of the effect of radiation on the precipitation of carbon in alpha-iron.

The effect of neutron irradiation at 25-30°C on the martensitic transformations in 47.5 and 50 at. % cadmium Au-Cd single crystals has been observed.

The crystallographic theory of cubic-tetragonal martensitic phase changes has been generalized, and the expressions that result are used to establish criteria for the degeneracy of solutions. Furthermore, a graphical method is used to investigate the consequences of the assumption of a lattice invariant shear on the close-packed planes of the cubic structure.

SEMICONDUCTOR STUDIES

Disordered Regions in Semiconductors

A model for the potential well surrounding disordered regions in neutron-irradiated germanium and silicon is discussed.

Fermi Level Spectrometry

Thermal neutron irradiation of germanium alters the extrinsic carrier concentration by defect formation as a result of recoil following neutron absorption and by the formation of chemical impurities resulting from transmutations. This process permits a form of nuclear doping that can alter the position of the Fermi energy level. Some preliminary experiments are described wherein this technique is utilized to examine the position and electrical role of reactor- and Co⁶⁰-gamma-ray-introduced energy levels.

Nature of Bombardment Damage and Energy Levels in Semiconductors

The different effects of Co⁶⁰-gamma-ray and fast-neutron bombardment on the electrical behavior of germanium are discussed in terms of the distribution of lattice defects.

Thermal Neutron Capture in Silicon and Germanium

The absorption cross section, kinetic energy of recoil, formation of donor and acceptor impurities, and effect on electrical properties are both estimated and compared with experiments.

Radiation Effects on Carrier Recombination in Germanium

The effect of neutron and gamma irradiation upon minority carrier lifetime has been studied. The results of these studies are summarized. Annealing studies using lifetime measurements as a measure of the damage present are being initiated.

Monoenergetic Neutron Irradiation of Germanium

The effect of 14-Mev-neutron irradiation upon the electrical properties of germanium has been studied, using lifetime, Hall coefficient, and resistivity measurements to determine the nature of the radiation-produced defects.

Thermoelectric Power in Germanium

Measurements of an unirradiated, *n*-type germanium crystal agree well with previous work on

impure polycrystalline material. Phenomena previously attributed to experimental factors are still seen when these factors are removed. A dependency of thermoelectric power on ΔT is observed. A preliminary study has been made of the change in thermoelectric power of *n*-type germanium as a result of neutron irradiation. The measurements were made for the temperature range between -50 and -70°C . A pronounced change in both the magnitude and the temperature dependence was observed.

Annealing of Radiation Effects in Germanium

Annealing of radiation-induced conductivity changes in *n*-type germanium was found to take place in the range between 77 and 273°K . The fractional recovery was about 6% in the samples studied, regardless of the total amount of radiation-induced change or relative amount of induced change. The resolution of data for large, relative, induced changes indicates the possibility of a quantitative study of the annealing in this temperature range.

Radiation Effects on Plastically Deformed Germanium

The dislocation density of germanium can be altered by plastic deformation. Annealing results on Co^{60} -gamma-ray-irradiated germanium have suggested preferential migration of interstitials. The effect of initial dislocation density on interstitial migration has been investigated.

Hall Mobility of Irradiated Germanium

The charge-center concentration as a function of temperature of high-purity, *n*-type germanium under fast-neutron irradiation is compared to similar data obtained for Co^{60} gamma-ray irradiations.

The Diffusion of Copper in Germanium

The diffusivity, solid solubility, and acceptor behavior of copper in germanium is being investigated. Radiation studies using carrier concentration to ascertain the position of the energy levels introduced by the copper acceptor states are being initiated.

Effect of Neutron Spectrum on Conductivity Change in Germanium

Neutron flux measurements were compared with conductivity changes in *n*-type germanium for a

donut hole and a well-moderated hole. The marked influence of the low-energy flux indicates a saturation of the conductivity change vs neutron energy starting at about 0.2 Mev.

Gamma Irradiation of *n*-Type Silicon

Hall coefficient and Hall mobility have been measured as a function of temperature and Co^{60} gamma-ray irradiation on a number of *n*-type silicon samples. A trapping level located 0.17 ev below the conduction band is evident in all the samples. From the introduction rate of this level and the Fermi level in the material, it is tentatively concluded that the process of formation of the level may be affected by the density of donors in the original material.

Magnetism of Interacting Donors

The magnetic susceptibility of donor centers in semiconductors is calculated for the case of small interactions between closely adjacent donors. A hydrogenic model is assumed for the donor centers. The random distribution of the centers, as well as the variation of the energy of interaction with separation distance of pairs of donors, is taken into consideration. A twofold modification to the Curie law (which is correct for independent donors) is predicted by the resulting expression, namely, a curvature as well as a decrease of the slope of the Curie plot of the susceptibility vs inverse temperature. Both of these effects increase with the donor density, becoming appreciable in silicon with 10^{17} – 10^{18} donors/cm³ and in germanium in the range around 10^{16} donors/cm³. The theory is in good agreement with results of measurements.

Magnetic Susceptibility of Aluminum Antimonide

Preliminary measurements of the magnetic susceptibility of AlSb indicate more complicated behavior than has been observed in silicon and germanium.

INSULATING CRYSTALS

Fast-Neutron and Gamma Coloration in KCl

Both types of radiation produce an optical absorption band at $2140 \text{ \AA}$ which bleaches with continued irradiation in the initial rapid rise in *F*-band coloration (stage I). In stage II, the *F*-band and *V*-band growth rates are lower and constant. Any adjustment of reactor to Co^{60} irradiation time

indicates a neutron effect for both *F*-band and *V*-band development. In stage III the growth rates are less than in stage II. Though neutron irradiation produces a coloration with a maximum at 2140 Å and gamma irradiation a maximum at 2080 Å, the difference between these spectra indicates a maximum at 2300 Å. This maximum increases in intensity with irradiation.

Vacuum Ultraviolet Absorption Studies of Irradiated Silica and Quartz

The most prominent optical absorption band developed in irradiated fused silica and crystalline quartz in the spectral range below 2000 Å has a maximum at 7.65 eV (1620 Å). The effects of optical and thermal treatments indicate that this band is not complementary to a band at 5.9 eV (2100 Å) as is normally assumed. Other absorption bands appear at 8.05 and 8.20 eV. The results of optical and thermal treatments as well as curve fitting suggest other absorption bands at 7.25, 7.40, 7.85, and 7.95 eV.

Irradiation Effects and Short-Range Order in Silica and Quartz

From a comparison of the envelope shape of an electron spin resonance line observed in gamma-ray-irradiated silica with the envelope shape calculated from the single-crystal parameters of this line, a degree of short-range order is suggested extending over a region ≥ 5 Å in diameter. A further comparison with the envelope shape observed in heavily neutron-irradiated silica or quartz indicates an alteration of this order. Annealing experiments show a recovery of this order prior to the density recovery.

Irradiation Effects in Nonmetallic Crystals

Nonmetallic crystals with a variety of structures and chemical compositions have been exposed to fission-spectrum neutrons in core positions of the LITR and examined by x-ray diffraction techniques. Wherever possible, single crystals were employed, and the neutron dosages ranged between 10^{15} and 10^{21} neutrons/cm² at a temperature of approximately 85°C. In no case was a special technique used for examining radioactive materials, because the problem of heavy induced radioactivity was greatly reduced by working with crystals weighing a milligram or less. Film and counter measurements were employed.

Some of the more important conclusions reached as a result of these investigations are the following:

1. Crystals containing a high degree of covalent binding appear to be more susceptible to radiation effects than, say, ionic or metallic crystals.
2. If the crystal structure is anisotropic and if positive effects are produced by irradiation, then the effects are likely to be anisotropic as well.
3. Where several allotropic forms of a given substance can exist neutron irradiation sometimes stabilizes the high-temperature form, and this phase reversal may be stable up to temperatures approaching the melting point.
4. Some crystals which suffer volume changes as high as several per cent after irradiation still possess macroscopic integrity.
5. The fact that a given crystal appears unaffected by some finite irradiation dosage does not preclude the possibility that damaging effects may be observed as a result of dosages which are larger by an order of magnitude or more.

Fission Fragment Damage in Zirconia

Fission fragments were observed to cause a phase transition of monoclinic ZrO₂ to the cubic form. The measurements indicated that each fission fragment affected $\sim 10^6$ atoms in what is believed to be a "fission spike" mechanism. Pure monoclinic ZrO₂ remains stable in fast-neutron fluxes as high as 3.6×10^{20} nvt.

Magnetic Susceptibility of Potassium Rhenium Chloride

The temperature dependence of the magnetic susceptibility of K₂ReCl₆ has been measured between room temperature and 5°K. Above 60°K the data may be fitted by a Curie-Weiss law; however, at low temperatures large deviations occur. There seems to be little correlation between these deviations and specific heat anomalies, which occur above 75°K.

POLYMERS AND CERAMICS

The decrease in molecular weight of polymethyl methacrylate after irradiation has been followed for periods up to 500 hr. The magnitude and time dependence of the molecular weight change was the same whether the samples had been outgassed at room temperature or at 140°C, prior to irradiation. This indicated that the postirradiation change was caused by a reactive radiation product

rather than by unstable oxidation products. Two possible reaction mechanisms involving free radicals were applied to the data, but equations using reaction constants available from the literature were not satisfactory. For practical testing purposes it was noted that heating to 80°C for 1 hr, followed by aging for 24 hr at room temperature, *in vacuo*, brings the molecular weight to within 5% of the value reached after 500 hr of aging at room temperature.

The irradiation of specimens of polystyrene of 0.010 and 0.080 in. thickness indicates that the thin specimens undergo cross-linking at a greater rate than the thick specimens. This thickness effect is of the same order of magnitude as the acceleration of cross-linking by the orientation of the polymer molecules, but the dose dependence of the two effects is not the same. Exposure of irradiated specimens to air for various periods has revealed that postirradiation oxidation is not responsible for the observed effect.

Deuterated basic beryllium acetate complex has been irradiated for doses up to 2.9×10^{22} ev/g (4.6×10^8 rads) at a thermal-neutron flux of 6×10^{11} neutrons $\cdot$ cm $^{-2}$ $\cdot$ sec $^{-1}$ to give neutron doses up to 1.6×10^{18} neutrons/cm 2 . The total gas evolution was 0.52 molecule per 100 ev of absorbed energy, and the evolution of gas not condensed at -190°C was 0.41 molecule per 100 ev. A decrease in melting point as a consequence of irradiation was observed. The change in melting point was linear with radiation dose, decreasing from the initial value of 287°C to 251°C at the maximum dose, 2.9×10^{22} ev/g. Irradiation produced no change in the x-ray diffraction pattern of the samples.

The effect of an exposure of 2×10^{20} *nv* (thermal) in the ORR on the thermal stability of Cassiar, Thetford, crocidolite, and amosite asbestos was studied. Since there was not much change, this study will be extended to higher exposures. Greater weight loss was observed for the Thetford and crocidolite materials.

The energy absorbed in hydrogen and carbon from fast neutrons and gamma rays was calculated from calorimetric measurements made in Holes 19 and 51 of the ORNL Graphite Reactor. Corrections from thermal-neutron reactions are described and are smallest inside the uranium converter in Hole 51. Comparison with calculations from neutron flux measurements shows better agreement with

the calorimetric value, for the case of the converter.

RELATIVE EFFICIENCIES OF NEUTRONS AND GAMMA RAYS IN POLYMER IRRADIATION EFFECTS

Polymers were irradiated in a reactor and a cobalt gamma-ray source. The results, when compared with calorimetric measurements, determine the relative efficiencies for fast neutrons and gamma rays. The cleavage reactions in polymethyl methacrylate and polyisobutylene have lower efficiencies for fast neutrons than for gamma rays, and the gassing reactions in allyl diglycol carbonate, nylon, and polyethylene have higher efficiencies for fast neutrons.

EVALUATION OF THE ORNL GRAPHITE REACTOR

A stored energy evaluation of the ORNL Graphite Reactor indicated that no unduly hazardous condition existed. It was shown that less than 5% of the moderator volume was capable of undergoing a spontaneous energy release.

CRYOSTAT FOR HOLE 50, ORNL GRAPHITE REACTOR

A cryostat was installed in Hole 50 of the ORNL Graphite Reactor. Irradiations may be conducted at temperatures approaching that of liquid nitrogen in a flux field of about 3×10^{11} *nv_f* and 7×10^{11} *nv_{th}* at a reactor power at 3400 kw. Samples may be inserted and removed during reactor operation.

HIGH-TEMPERATURE REACTOR FUELS

An irradiation program is well under way to evaluate the stainless-steel-canned UO $_2$ fuel element for the Experimental Gas-Cooled Reactor (EGCR). Postirradiation examinations include measurement of fission gas release and structural stability. Two additional experiments were constructed in the ORR: one for instantaneous fission gas release studies and the other for studies of advanced fuel materials.

A high-temperature oxidation-resistant cladding (SiC-Si) for graphite was studied for thermal and radiation stability. The thermocouple irradiation program was completed and calibration deviations established for Chromel-Alumel and platinum vs platinum-10% rhodium couples.

BRITTLE FRACTURE OF METALS

A new program to study irradiation embrittlement of metals was begun. The mechanical properties of high-purity iron and iron-carbon alloys will be determined as a function of material and test parameters in order to conduct later irradiation experiments, particularly at elevated temperatures, with stable materials.

RADIATION METALLURGY

Commercial carbon steels irradiated at temperatures up to 330°F exhibited a rise in notch-impact transition temperature that is linear with the logarithm of the fast-neutron dose from 10^{18} to

10^{20} *nvt* (>1 Mev). Greater change was observed for a quenched and tempered alloy steel and lesser change for a high-purity iron-carbon alloy. Data for three steels indicated that irradiation at 390°F is less damaging than at less than 200°F. Other data indicates greater damage at 270 and 440°F than at less than 200°F.

Tube-burst tests on Inconel are continuing in the ORR. The rupture lives are similar to those observed in the last MTR experiment: a factor of 3 to 5 lower than the out-of-pile rupture lives. It is suggested that the presence of boron and its nuclear transmutation products (helium and lithium) may be responsible for these results. An in-pile stress-rupture program on beryllium has been initiated.

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THEORY OF RADIATION DAMAGE

CLASSICAL SCATTERING THEORY FOR INTERATOMIC COLLISIONS

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An adequate understanding of the effects of irradiation on solids must eventually be based upon the knowledge of the complete collision histories of the primary, secondary, etc., knock-ons. The collision histories are determined by the details of the single collision process between a moving lattice atom and a stationary lattice atom. Finally, the collision process is determined by the interatomic potential. It is the fact that so little is known of the interatomic potential which has held up progress in the theoretical understanding of radiation damage. This potential cannot at the present time be obtained practically by direct calculation from the principles of quantum mechanics; further, experiments which could give information on the form of the potential are just now beginning to be considered.^{2,3} Some calculations have already been attempted on the basis of assumed forms of the potential, with the hope of interpreting preliminary experimental results. In particular, Nielsen⁴ has considered a potential of the C/r^2 form with special choices for C ; and two of the present authors have considered⁵ the form taken by Bohr, that is,

$$V(r) = \frac{E_B e^{-r/a}}{2r/a}, \quad (1)$$

where

$$E_B = \frac{2Z^2 e^2}{a}, \quad (2)$$

and a = the screening radius. Neither of these calculations is internally consistent since, for purposes of making the calculation feasible, an approximate angular distribution, namely, the "hard-core approximation," was assumed and used along with the exact spatial dependence of the particular potential function.

The present investigation was begun with the purpose of estimating the error introduced by the use of the approximate angular distribution and with some hope of discovering a more exact method of calculation. It is now felt, however, that the work has a greater importance for the broader problems. It seems clear that the scattering of atoms with energies in the 100- to 100,000-ev range by identical stationary atoms will continue to be a basic problem in radiation damage. It also seems certain that treatment by classical mechanics, as used here, is sufficiently accurate. Thus, the experience gained

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²R. A. Schmitt and R. A. Sharp, *Phys. Rev. Letters* **1**, 445 (1958).

³M. I. Guseva, E. V. Inopin, and S. P. Tsytko, *Soviet Phys. JETP* **36**(1), 1 (1959).

⁴K. O. Nielsen, in *Electromagnetically Enriched Isotopes and Mass Spectrometry*, Academic Press, Inc., New York, and Butterworth, London, 1956.

⁵D. K. Holmes and G. Leibfried, "The Range of Radiation Induced Primary Knock Ons in the Hard Core Approximation," to be published in *J. Appl. Phys.* See abstract, this report.

in this investigation can be of great value in utilizing the increased knowledge of the interatomic potential as it is gained. Further, certain results can be obtained which are applicable for a wide range of potentials. The present discussion is only a preliminary report of the current study of this problem.

The Classical Scattering Integral

The collision between two like atoms⁶ is describable classically by the following equations:⁷

$$\Theta = \pi - 2p \int_0^{u_0} \frac{du}{\sqrt{1 - (2V/E) - p^2 u^2}}, \quad (3)$$

$$T = E \sin^2 \frac{\Theta}{2}, \quad (4)$$

$$\kappa(T) = -\frac{4\pi}{E \sin \Theta} p \frac{dp}{d\Theta}, \quad (5)$$

with the following definitions:

Θ = the scattering angle in the center-of-mass system.

$V(r)$ = the interatomic potential as a function of atomic separation, $u = 1/r$. (Consideration is restricted here to monotonic potentials.)

u_0 is defined by

$$1 - \frac{V(u_0)}{E} - p^2 u_0^2 = 0. \quad (6)$$

E = the initial kinetic energy of the moving atom.

p = the impact parameter.

T = the kinetic energy transferred to the struck atom.

$\kappa(T)dT$ = the cross section for energy transfers in the range $(T, T + dT)$.

One other definition will be useful in the following discussion:

R $\equiv$ the distance of closest approach is defined by

$$\frac{E}{2} = V(R). \quad (7)$$

A few points with respect to this set of equations are worth noting. First, the description is precise within the framework of classical mechanics; and its applicability to the present problem depends on the knowledge of the potential function, $V(r)$. Second, the integral of Eq. (3) can be explicitly performed in

⁶Throughout the following we will consider only collisions between equal masses, the most important case for elemental solids. However, the results may be readily extended to cover encounters in which the masses are unequal.

⁷H. Goldstein, *Classical Mechanics*, p 73, Addison-Wesley, 1950.

terms of closed functions only in a few special cases, discussed later; and, in general, numerical techniques are required. Third, a very large value of the impact parameter corresponds to passage of the incident particle at a very large distance from the stationary atom, thus to a small angle of scattering and a small energy transfer. Conversely, a value of p near zero corresponds to a nearly head-on collision, thus to a scattering angle, Θ , near π , and a transfer of nearly all the kinetic energy of the moving atom to the struck atom. If the potential has a nonvanishing value for any separation less than infinity, no matter how large, the cross section $\kappa(T)$ diverges for large impact parameter, that is, small T ; and, further, the total cross section given by

$$\sigma = \int_0^E \kappa(T) dT \quad (8)$$

also diverges. That these divergences are not of physical importance may be regarded in two ways: (1) It may be that the actual interatomic potential (particularly in a lattice of atoms) essentially vanishes beyond a certain separation (e.g., in a lattice of atoms the lattice spacing itself serves as a natural limit for applicability of the interatomic potential); thus, the divergences in reality do not exist, and the proper representation of the potential is not the usual, continuous functional form, such as combinations of powers of r and exponentials, but rather the latter with some "cutoff" radius. (2) The divergence may be such that the collision history of an atom is not effectively different from that which would be predicted from the appropriate "cutoff" potential; thus, both histories would consist of many collisions of nearly zero energy transfer and a few of significant energy transfers. More quantitatively, it might be considered that the divergences of $\kappa(T)$ and σ are unimportant if

$$\int_0^E T \kappa(T) dT$$

is finite.⁸

The Elementary Cases

It may be worth while at this point to present the results of the use of potentials whose forms are such that the integral in Eq. (3) may be readily performed.⁹ These cases are: (1) a constant potential,

$$V(r) = V_0, \quad (9)$$

corresponding to no scattering; (2) the "hard-core" potential,

$$V(r) = \begin{cases} 0, & r > R_0, \\ \infty, & r \leq R_0, \end{cases} \quad (10)$$

⁸The corrections for small-angle deflections introduced by quantum mechanics serve to keep the properly calculated cross section finite. However, these corrections are important only for energy transfers even smaller than those excluded by a realistic cutoff of the potential.

⁹Note that we are restricting our considerations to repulsive potentials, which is expected to be appropriate to atomic scattering problems.

corresponding to the scattering from an impenetrable sphere; (3) the Coulomb potential,

$$V(r) = \frac{Z^2 e^2}{r}, \quad (11)$$

corresponding to the scattering of charged particles; and (4) the inverse r -squared potential,

$$V(r) = \frac{c}{r^2}, \quad (12)$$

which does not correspond to any known physical system. The results are summarized in Table 1.

The ratio tabulated in line 5 of Table 1 is of interest from the following viewpoint. The hard-core potential provides a mathematically simple form for the scattering law, thus suggesting the attractive possibility that the true potential may in some sense be replaced by the hard-core potential as a good approximation. As a first guess we try using for the approximating hard-core radius, $R(E)$, the distance of closest approach in a head-on collision, as given in Eq. (7). Then the ratio given in line 5 of Table 1 can be used to determine in what ranges, if any, the approximation is useful. Graphs of these three ratios are given in Fig. 1 (along with other curves, to be discussed later). Note that all three of these ratios depend only on T/E , the ratio of the transferred energy to the initial energy, and not on E alone. This is, of course, not true in general.

Line 9 of Table 1 gives the ratio of energy transferred per unit path length for the given potential to that for the hard-core potential, used as previously described. Note that the Coulomb potential is special among inverse-power-law potentials in giving a divergent result for this integral. This indicates that, to be realistic, the Coulomb potential must be modified or cut off in actual application.

Some General Properties of the Scattering Integral

The Cross Section Near the Limit of Maximum Energy Transfer. — In the limit of vanishing impact parameter, for which case the total energy, E , is transferred to the struck atom, it may be shown by consideration of the limit of Eq. (3) that the scattering angle approaches π in such a way that

$$\kappa(E) = \frac{\pi}{I_1^2 E}, \quad (13)$$

where I_1 is the following integral:

$$I_1 = \int_0^{1/R} \frac{du}{\sqrt{1 - (2V/E)}}; \quad (14)$$

R is defined by:

$$V(R) = \frac{E}{2}.$$

Table 1. The Elementary Cases

	Constant Potential	Hard-Core Potential	Coulomb Potential	Inverse r -Squared Potential
1. $V(r)$	V_0	$\begin{cases} 0, & r > R_0 \\ \infty, & r \leq R_0 \end{cases}$	$\frac{Z^2 e^2}{r}$	$\frac{c}{r^2}$
2. $R(E)^a$	b	R_0	$\frac{2Z^2 e^2}{E}$	$\sqrt{\frac{2c}{E}}$
3. $\Theta(p)$	0	$\begin{cases} 0, & p > R_0 \\ 2 \cos^{-1} \frac{p}{R_0}, & p \leq R_0 \end{cases}$	$2 \sin^{-1} \left(1 + \frac{p^2 E^2}{Z^4 e^4} \right)^{-1/2}$	$\pi \left[1 - \left(1 + \frac{2c}{Ep^2} \right)^{-1/2} \right]$
4. $\kappa(T)^c$	0	$\frac{\pi R_0^2}{E}$	$\frac{\pi Z^4 e^4}{E} \frac{1}{T^2}$	$\frac{\left(1 - \frac{2}{\pi} \sin^{-1} \sqrt{\frac{T}{E}} \right) \frac{4c}{E^2}}{\left[1 - \left(1 - \frac{2}{\pi} \sin^{-1} \sqrt{\frac{T}{E}} \right)^2 \right]^2 \sqrt{\frac{T}{E}} \sqrt{1 - \frac{T}{E}}}$
5. $\frac{E \kappa(T)}{\pi R^2(E)}$	b	1	$\frac{1}{4} \left(\frac{E}{T} \right)^2$	$\frac{2}{\pi} \frac{\left(1 - \frac{2}{\pi} \sin^{-1} \sqrt{\frac{T}{E}} \right)}{\left[1 - \left(1 - \frac{2}{\pi} \sin^{-1} \sqrt{\frac{T}{E}} \right)^2 \right]^2 \sqrt{\frac{T}{E}} \sqrt{1 - \frac{T}{E}}}$
6. $\frac{E \kappa(E)}{\pi R^2(E)}$	b	1	$\frac{1}{4}$	$\frac{4}{\pi^2}$
7. Small angle approximation to the ratio of line 5 ^d	b	e	$\frac{1}{4 \sqrt{\frac{T}{E}} \sqrt{1 - \frac{T}{E}} \left(\sin^{-1} \sqrt{\frac{T}{E}} \right)^3}$	$\frac{2}{\pi} \frac{1}{\left(\frac{4}{\pi} \sin^{-1} \sqrt{\frac{T}{E}} \right)^2 \sqrt{\frac{T}{E}} \sqrt{1 - \frac{T}{E}}}$
8. Momentum approximation to line 5	b	e	$\frac{1}{4} \left(\frac{E}{T} \right)^2$	$\frac{\pi}{8(T/E)^{3/2}}$
9. $\frac{\int_0^E T \kappa(T) dT}{(E/2) \pi R^2(E)}$	b	1	(Diverges logarithmically as the lower limit of the integral approaches zero)	~ 1.6

^aFrom Eq. (7).

^bThe constant potential case is unrealistic and is cited only for comparison.

^cThe form given applies only in the range $0 \leq T \leq E$.

^dThis is from the form of Eq. (17)

^eThe approximation scheme is not applicable to the hard-core potential.

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Fig. 1. Comparison of the Differential Scattering Cross Section as Calculated Exactly for the Coulomb, Inverse r -Squared, and Bohr Potentials, and as Approximated by the Cutoff Potential of Eq. (43).

This result gives the values shown in line 6 of Table 1. Also,

$$\frac{E \kappa'(E)}{\kappa(E)} = - \left(\frac{2}{3} - \frac{4I_2}{I_1^3} \right), \quad (15)$$

where

$$-I_2 = \int_0^{1/R} \frac{du}{\sqrt{1 - (2V/E)}} \left[\frac{u^2}{2} + V \frac{d}{du} \left(\frac{u^2}{dV/du} \right) \right] \quad (16)$$

The Cross Section for Low Energy Transfers. – In the limit of very large impact parameter, for which case the energy transfer becomes vanishingly small, it may be shown by direct manipulation of the integral of Eq. (3) that a first approximation is given by¹⁰

$$\Theta \approx \frac{2}{E} \int_0^{1/p} \frac{[-V'] du}{u \sqrt{(1/p^2) - u^2}} \approx \frac{2}{E} I_3. \quad (17)$$

In the integrand of Eq. (17)

$$V' \equiv \frac{dV}{dr} \quad (18)$$

¹⁰The mathematical treatment assumes that the potential is continuous and has a continuous first derivative over the infinite range.

and is to be taken as a function of $u \equiv 1/r$. For any specified potential, then, the cross section as a function of energy transferred may be obtained from Eqs. (4) and (5). The limits of validity of the "small-angle approximations" as given in Eq. (17) have not been properly examined. The terms neglected involve powers of the quantity a/p higher than 2, in comparison with the term retained, which is just of the second power in a/p . (Here a is some typical length for the potential.) However, the coefficients of the higher power of a/p have not been evaluated, so that one can only say that the approximation becomes better for larger impact parameter; and one cannot yet estimate the error in the approximation at any given value of a/p .

The "small-angle approximation" of Eq. (17) has an interesting relation to the "momentum approximation" commonly used in the limit of large impact parameter. This approximation is obtained by calculating the energy transferred to the moving atom (in the center-of-mass system) under the assumption that it moves in a straight line past the center of force at a distance p . Thus, the momentum transfer is computed from the knowledge of the impulse of the force perpendicular to the line of motion, with the effect of the deflection neglected. The result is an approximation for the energy transferred as a function of the impact parameter,

$$T(p) = \frac{I_3^2}{E}, \quad (19)$$

where I_3 is as defined in Eq. (17). From the general relationship of Eq. (3),

$$\sin \frac{\Theta}{2} = \frac{I_3(p)}{E}. \quad (20)$$

Thus, the two approximations [that of Eq. (17) and that of Eq. (20)] are not strictly identical; however, since both apply only in the range of small Θ , where $\sin (\Theta/2) \sim \Theta/2$, the differences are not important in the range of applicability. Unfortunately, the momentum approximation also does not afford an estimate of the error involved in its use. The approximating forms for both cases, for the cross sections using the two simple power potentials, are given in Table 1, lines 7 and 8. It is interesting to note that the momentum approximation [Eq. (20), used with Eq. (5)] is identical with the exact result for the Coulomb potential. For the inverse r -squared potential, the momentum approximation is again somewhat closer to the exact result than the small-angle approximation. In this case, however, the two approximations bracket the exact result, with the small-angle approximation giving the highest values for the cross section.

An Alternative Form for the Scattering Integral.¹¹ - With the help of Eq. (6) and a change of variable, the integral of Eq. (3) may be put in an alternative form:

$$\int_0^{u_0} \frac{du}{\sqrt{\frac{1}{p^2} - \frac{2V(u)}{Ep^2} - u^2}} = 2 \int_0^{\sqrt{u_0}} \frac{dx}{\sqrt{\frac{2}{Ep^2} \left[\frac{V(u_0) - V(u_0 - x^2)}{x^2} \right] + 2u_0 - x^2}}$$

The advantage of the second form is particularly great in numerical integration, which is necessary for more complex forms of the potential function. The second form avoids the difficulty of the divergence of the integrand at one limit, which is shown in the first form and which may be inconvenient for numerical work.

Some Results for Inverse Power Potentials

It seems worthwhile to investigate inverse power potentials more closely. The reason is that one can approximate any potential rather well by a power potential, at least over a limited range. The approximation is made as follows. The approximate potential, V_{app} , is chosen to agree in absolute value and in slope at the distance of closest approach, R , as defined by Eq. (7). Therefore, one has:

$$V_{app}(r) = V(R) \left(\frac{R}{r} \right)^n \quad (22)$$

and

$$V'_{app}(R) = -n \frac{V(R)}{R} = V'(R) \quad (23)$$

The last equality, then, determines the power, n ,

$$n = - \frac{RV'(R)}{V(R)} \quad (24)$$

For a potential of the Bohr type [Eq. (1)], one obtains

$$n = 1 + \frac{R}{a} \quad (25)$$

This approximation matches the true potential near the distance of closest approach and should give, therefore, dependable information about near head-on collisions and thus about transferred energies near E . Now n is a measure of the steepness of a potential for any given incident energy. The condition for hard-core scattering is essentially

$$n \gg 1 \quad (26)$$

Thus, one can anticipate a close resemblance to the hard-core behavior for large n .

¹¹Originally suggested by H. C. Schweinler.

For power potentials, the integrals I_1 and I_2 of Eqs. (14) and (16) can be easily calculated. The results are:

$$I_1^{(n)} = \frac{1}{nR} \frac{\Gamma\left(\frac{1}{n}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)} \quad (27)$$

and

$$I_2^{(n)} = \left(\frac{1}{2} - \frac{3}{n}\right) \frac{1}{nR^3} \frac{\Gamma\left(\frac{3}{n}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{1}{2} + \frac{3}{n}\right)}. \quad (28)$$

Thus, the ratio of $\kappa_n(E)$ to the hard-core value is given by

$$\frac{E \kappa_n(E)}{\pi R^2} = \frac{1}{(I_1 R)^2} = \left\{ \frac{n \Gamma\left(\frac{1}{2} + \frac{1}{n}\right)}{\Gamma\left(\frac{1}{n}\right)\Gamma\left(\frac{1}{2}\right)} \right\}^2. \quad (29)$$

For large n one gets the expansion

$$\frac{E \kappa_n(E)}{\pi R^2} = 1 - \frac{4 \ln 2}{n} \approx 1 - \frac{2.8}{n}, \quad (30)$$

which shows that really $\kappa_n(E)$ approaches the hard-core value only rather slowly with increasing n . The behavior of this ratio with n is shown in Fig. 2.

Fig. 2. The Comparison of the Cross Section for Maximum Energy Transfer in an Inverse Power Potential with the Corresponding Hard-Core Value as a Function of the Power of r in the Potential.

Also included in Fig. 2 are some corresponding values obtained from the numerical work (to be described in the next section) for the Bohr potential. Using the known values of R/a obtained from the chosen values of E , using Eqs. (1) and (7), the appropriate value of n at which the ratio of the cross sections is to be plotted may be obtained from Eq. (25).

Since the limit of the expression

$$\frac{\alpha \Gamma\left(\frac{\alpha}{n}\right) \Gamma\left(\frac{1}{2}\right)}{n \Gamma\left(\frac{1}{2} + \frac{\alpha}{n}\right)}$$

for large n is unity, one can easily see that the limiting value of I_2 is $1/[6(nR)^3]$ and that the limiting value of I_1 is $1/nR$. Thus, according to Eq. (15), $\kappa'_n(E)$ tends toward zero with increasing n , showing the resemblance to the hard-core approximation. Table 2 gives some specific values for $E \kappa'_n(E)/\kappa_n(E)$. As may be seen, even for $n = 10$, the slope is still appreciable.

Though the study of the momentum approximation for power potentials is of little value for the present problem, since it is felt that the Bohr potential of Eq. (1) is a better representation of the true potential for the energy range of interest and that power potentials cannot fit well with an exponentially decreasing potential except over a short range, some results in the momentum approximation are given here for comparison with the hard-core approximation. The integral I_3 of Eq. (17) can be evaluated for any function, $V(r) = \text{const}/r^n$; and, using Eq. (19), we obtain

$$p^2 = R^2 \left(\frac{E}{4T} \right)^{1/n} C_n^{2/n}, \quad (31)$$

with

$$C_n \approx \frac{\Gamma\left(\frac{n+1}{2}\right) \Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{n}{2}\right)}. \quad (32)$$

Table 2. The Slope of the Cross Section at Maximum Energy Transfer for Inverse Power Potentials

$n = \text{Inverse Power of } r$	$E \kappa'_n(E)/\kappa_n(E)$
1	2.
2	1.47
3	1.16
4	0.93
5	0.72
10	0.57

This gives for the differential cross section, using Eqs. (4) and (5):

$$\frac{E \kappa_n^{(\text{mom})}(T)}{\pi R^2} = \left(\frac{E}{T}\right)^{1+(1/n)} \frac{C_n^{2/n}}{(4^{1/n})n}. \quad (33)$$

One would expect that the hard-core approximation for large n would be rather good for values of T larger than T' given by

$$\frac{E \kappa_n^{(\text{mom})}(T')}{\pi R^2} = 1, \quad (34)$$

or, from Eq. (33),

$$\frac{T'}{E} = \frac{C_n^{2/(n+1)}}{4^{1/(n+1)} n^{n/(n+1)}}. \quad (35)$$

It is easy to see that T'/E for large n is essentially determined by the term $n^{n/(n+1)} \sim n$ in the denominator, and, thus, for large n it is seen that the energy range where the hard-core approximation may be useful is rather large.

Numerical Results Using the Bohr Potential

The screened Coulomb potential, as given in Eq. (1), is especially interesting for the present class of problems since there is reason to suppose that over some of the energy range the actual interatomic potential may be well represented by that form. This potential and the choice of the screening parameter have been previously discussed.⁵ The point of interest here is the exact calculation of $\kappa(T)$ for this potential. In the previous discussion⁵ the form $\kappa(T)$ was taken to be that of the hard-core approximation with the appropriate radius; thus, as a suggested approximation,

$$\kappa(T) = \frac{\pi R^2(E)}{E}, \quad 0 \leq T \leq E, \quad (36)$$

with $R(E)$ defined by

$$\frac{E}{2} = \frac{E_B}{2} \frac{e^{-R/a}}{R/a}. \quad (37)$$

The use of this approximate form is attractive because its simplicity allows for explicit evaluation of certain averages over the collision history of the moving atom; however, it is, of course, important to try to evaluate the validity of this approximation.

The calculation of $\kappa(T)$ from Eqs. (1)–(5) for the Bohr potential form was performed numerically on the Oracle at ORNL. The results for the specifically interesting ratio, $E \kappa(T)/\pi R^2(E)$, are shown in Fig. 3. The result, of course, depends on the value of E chosen; the various choices made are indicated in Fig. 3 by the appropriate value of R/a as obtained from Eq. (37) once E has been specified.

Fig. 3. The Ratio of the Cross Section per Unit Energy Range to the Hard-Core Cross Section for the Bohr Potential for Various Energies as a Function of Transferred Energy.

A typical one of these curves is included in Fig. 1 and compared with the κ 's for the Coulomb and inverse r -squared potentials. It is to be noted that the ratio chosen [namely, to $\pi R^2/E$, where R is calculated from Eq. (7) for each potential] is independent of E for the two elementary potentials.¹² For the cases $R/a = 3.4$ and $R/a = 5.25$, the curves shown include all the values calculated to date.

With respect to the original problem of the error involved in the hard-core approximation and also with respect to the larger problem of using the true cross-sectional form in a more exact calculation, no firm conclusions have been achieved at this time. The cross-section curves for low energies

¹²As a help in interpreting Fig. 3, it may be mentioned that for copper, $E_B \sim 10^5$ ev, so that $R/a \sim 0.35$ corresponds to $E \sim 2 \times 10^5$ ev; $R/a \sim 1$ corresponds to $E \sim 30,000$ ev; $R/a \sim 3.4$ corresponds to $E \sim 1000$ ev; and $R/a \sim 5.25$ corresponds to $E \sim 100$ ev.

($R/a = 3.4$ and 5.25 , for example) do not lie as closely to the hard-core form as had been hoped before the calculation was performed. On the other hand, the significance of the error is not known.

It is of interest to compare the exact results with the momentum approximation. For the Bohr potential form, the integral I_3 of Eq. (17) is related to the hyperbolic Bessel function K_1 , as shown by Brinkman;¹³ the precise result corresponding to Eq. (19) for the potential of Eq. (1) is:

$$\frac{T(p)}{E} = \frac{E_B^2}{4E^2} K_1^2\left(\frac{p}{a}\right). \quad (38)$$

The cross section may be calculated from Eqs. (4) and (5), with the result:

$$\frac{E \kappa(T)}{\pi a^2} = \frac{4E^2}{E_B^2} \frac{p/a}{F(p/a)}, \quad (39)$$

where

$$F(x) = K_1(x) K_0(x) + \frac{K_1^2(x)}{x}. \quad (40)$$

In Fig. 4, the ratio calculated from Eq. (39)¹⁴ is shown in comparison with the same ratio as numerically evaluated for the same choices of E_B/E . It is clear from Fig. 4 that, while the momentum approximation is better for small values of T/E , it is not possible to make a general statement as to the error. It appears that it is not even possible to be sure whether the approximation is greater or smaller than the exact value, since both cases are found for different values of E and sometimes both cases can be found in different ranges of T/E for a single value of E . It does seem that the approximation is poorer for the low energies ($R/a > 1$), where it was hoped that the approximation could be used to supplement the numerical work. The small-angle approximation is generally not quite as good as the momentum approximation, over the range in which the two differ.

Some Aspects of Scattering Using Cutoff Potentials and Matching Potentials

It has been pointed out previously in this report that perhaps a more realistic scattering potential for interacting atoms is one which goes to zero at some finite distance of separation. The point of view taken is to investigate these cutoff potentials in order to try to get more information about the real scattering, which is presumably well represented by the Bohr potential. For instance, this procedure should be more accurate than the hard-core approximation to the Bohr potential.

¹³J. Brinkman, *J. Appl. Phys.* **25**, 961 (1954).

¹⁴The actual values of the Bessel functions were used for the results of Fig. 4, using *Bessel Functions, Part I*, Cambridge University Press, New York, 1958. The asymptotic forms for the Bessel functions, using only the first terms, are not sufficiently accurate over the range of interest.

Fig. 4. The Momentum Approximation to the Cross Section in Comparison with the Calculated Values for the Bohr Potential Form. The numbers beside the curves give the R/a values.

With a cutoff potential of the form

$$V = \begin{cases} V(r) , & r \leq r_1 , \\ 0 , & r > r_1 , \end{cases} \quad (41)$$

the scattering integral [Eq. (4)] becomes

$$\Theta = \begin{cases} \pi - 2 \sin^{-1} pu_1 - 2p \int_{u_1}^{u_0} \frac{du}{\sqrt{1 - \frac{2V}{E} - p^2 u^2}} , & p \leq r_1 , \\ 0 , & p > r_1 , \end{cases} \quad (42)$$

where $u_1 = 1/r_1$. It is seen that the integral in Eq. (42) is the same as in Eq. (3), except that the lower limit is now u_1 rather than zero. Thus, one is still faced with intractable integrals, except for a few simple potential functions.

To date, preliminary work has been done using two different cutoff potentials¹⁵ in which the integral [Eq. (42)] can be done analytically. With a potential of the form

$$\frac{V}{E/2} = \begin{cases} C_3(r_1^2 - r^2) , & r \leq r_1 , \\ 0 , & r > r_1 , \end{cases} \quad (43)$$

the differential cross section is

$$\kappa(T) = \frac{\pi}{EC_3} \frac{\left[1 + C_3^2 r_1^4 - 8 \left(\frac{T}{E} - \frac{T^2}{E^2} \right) \pm 2 \sqrt{C_3^2 r_1^4 - 4 \left(1 + C_3^2 r_1^4 \right) \left(\frac{T}{E} - \frac{T^2}{E^2} \right) + 16 \left(\frac{T}{E} - \frac{T^2}{E^2} \right)^2} \right]^{3/2}}{C_3^2 r_1^4 - 4 \left(\frac{T}{E} - \frac{T^2}{E^2} \right) \pm \sqrt{C_3^2 r_1^4 - 4 \left(1 + C_3^2 r_1^4 \right) \left(\frac{T}{E} - \frac{T^2}{E^2} \right) + 16 \left(\frac{T}{E} - \frac{T^2}{E^2} \right)^2}} , \quad (44)$$

where the positive square root is taken if $T/E < 1/2$ and the negative square root when $T/E > 1/2$. It is

¹⁵A third potential has not yet been investigated but seems to provide a close fit to the Bohr potential; this potential has for the first part of Eq. (41), $V(r) = (c_1/r^2) - (c_2/r)$.

seen that in the limit of small energy transfers, $T \rightarrow 0$, the above cross section becomes

$$\frac{\pi}{C_3} \frac{(C_3 r_1^2 + 1)^2}{C_3 r_1^2}$$

and thus remains finite. The parameters C_3 , r_1 can be determined by matching this potential and its first derivative with the Bohr potential at the distance of closest approach. This has been done for the case when the ratio R/a of the Bohr parameters is 1.05, and the resulting scattering cross section is shown in Fig. 1.

It is interesting to apply the momentum approximation to determine the scattering from the above potential. It is expected that the momentum approximation will be good for small deflections corresponding to $p \sim r_1$. However, it is found that the limit of $\Theta_{\text{approx}}/\Theta_{\text{exact}}$ becomes $1 + C_3 r_1^2$ as the deflection angle approaches zero. It is seen, therefore, that the momentum approximation breaks down even in the limit of zero scattering angle unless $C_3 r_1^2$ is zero. However, the case of $C_3 r_1^2 = 0$ is unrealistic since it corresponds to zero scattering potential; and, moreover, from the matching of the above potential with the Bohr potential at the distance of closest approach, it can be shown that $C_3 r_1^2$ is always greater than unity. It is concluded that it is necessary to exercise caution when applying the momentum approximation, at least when dealing with cutoff potential fields.

Another cutoff potential which is currently being studied is

$$V = \begin{cases} C_1 + C_2 r^2 + C_3/r^2 & , \quad r \leq r_1 \\ 0 & , \quad r > r_1 \end{cases} \quad (45)$$

The scattering integral [Eq. (42)] can also be done analytically, using the above potential. The above function has three parameters; therefore, it is possible to match the potential, with its first and second derivatives, with the corresponding quantities of the Bohr potential. Thus, one should get a scattering cross section which agrees more closely with the Bohr scattering than that from Eq. (44), which has only two parameters.

The matching of potentials at the distance of closest approach, where this distance is that occurring in a head-on collision, has been discussed in a previous section of this report. An alternative way of matching potentials is to match them at the minimum orbital distance of approach, where this distance depends on the impact parameter and reduces to the distance of closest approach for the case of head-on collisions.

To illustrate the method, the scattering from a C_2/r^2 potential has been approximated by that of a C_1/r potential, where C_1 is a parameter adjusted to match the potentials at the point of closest approach in the orbit corresponding to a particular impact parameter.

For a Coulomb potential, the relationship between the impact parameter and the transferred energy is

$$p^2 = \frac{C_1^2}{E^2} \left(\frac{E - T}{T} \right) \quad (46)$$

and the scattering cross section is

$$\kappa_1(T) = -\pi \frac{dp^2}{dT} = \frac{\pi C_1^2}{ET^2} - \frac{\pi}{E^2} \left(\frac{E - T}{T} \right) \frac{dC_1^2}{dT} = \kappa_2(T) - \frac{\pi}{E^2} \left(\frac{E - T}{T} \right) \frac{dC_1^2}{dT} \quad (47)$$

In Eq. (47) the first term in $\kappa_1(T)$ has been recognized as the form of the differential scattering cross section for the pure Coulomb case and called $\kappa_2(T)$, for convenience. The relationship between C_1 and C_2 is found by matching potentials at the point r_0 ; thus,

$$\frac{C_1}{r_0} = \frac{C_2}{r_0^2}, \quad (48)$$

where r_0 is defined by

$$1 - \frac{2}{E} \frac{C_2}{r_0^2} - \frac{p^2}{r_0^2} = 0 \quad (49)$$

Equations (48) and (49) give

$$p^2 = \frac{C_2}{E} \left(-1 + \sqrt{\frac{E}{T}} \right), \quad (50)$$

and for the differential cross section

$$\kappa_1(T) = -\frac{C_2}{2T^{3/2}\sqrt{E}}, \quad \kappa_2(T) = \frac{C_2}{T^2(1 + \sqrt{E/T})}, \quad (51)$$

while the exact cross section for the C_2/r^2 potential is

$$\kappa(T) = \frac{4C_2}{E^2} \frac{\left(1 - \frac{2}{\pi} \sin^{-1} \sqrt{T/E} \right)}{\left[1 - \left(1 - \frac{2}{\pi} \sin^{-1} \sqrt{T/E} \right)^2 \right]^2 \sqrt{T/E} \sqrt{1 - (T/E)}} \quad (52)$$

Comparing the ratio of the approximations to the exact scattering for two limiting cases of energy transfers, one gets

$$\begin{aligned} \lim_{T \rightarrow 0} \frac{\kappa_1(T)}{\kappa(T)} &\rightarrow \frac{2}{\pi}, & \lim_{T \rightarrow T_n} \frac{\kappa_1(T)}{\kappa(T)} &\rightarrow \frac{\pi^2}{16}, \\ \lim_{T \rightarrow 0} \frac{\kappa_2(T)}{\kappa(T)} &\rightarrow \frac{4}{\pi}, & \lim_{T \rightarrow T_n} \frac{\kappa_2(T)}{\kappa(T)} &\rightarrow \frac{\pi^2}{16}, \end{aligned} \quad (53)$$

and the ratio of stopping power of the approximations to the exact gives

$$\frac{\int_0^E T \kappa_1(T) dT}{\int_0^E T \kappa(T) dT} = 0.63, \quad \frac{\int_0^E T \kappa_2(T) dT}{\int_0^E T \kappa(T) dT} = 0.88. \quad (54)$$

It is seen that this method is fairly good, at least for the two limiting cases of energy transfers and, also, for the stopping power. It is also seen that the function κ_2 seems to be better than κ_1 in approximating κ . The reason for this is not clear; in fact, it is difficult to interpret the physics involved in the approximation κ_2 .

CROSS SECTIONS FOR ATOMIC DISPLACEMENTS IN SOLIDS BY GAMMA RAYS

O. S. Oen D. K. Holmes

During the past year we have calculated cross sections for atomic displacements in solids by gamma rays. Some of this work appears in the *Journal of Applied Physics*, and an abstract is given below. Besides the published information we have calculated the displacement cross sections for atomic numbers 6, 13, 22, 40, 50, and 74; graphs of these are available from the authors upon request.

Cross Sections for Atomic Displacements in Solids by Gamma Rays.¹⁶ O. S. Oen and D. K. Holmes. — Cross sections for the displacement of lattice atoms by gamma rays for energies up to 5 Mev have been calculated. The principal contribution is found to come from the Compton effect, in which the atoms are displaced by electrons produced by the incident gamma rays. The calculations have been based on the assumption of a sharp threshold energy for displacement, but cross sections have been computed as a function of the assumed threshold energy. Thus, from the present work it is relatively easy to obtain cross sections based upon other displacement functions.

¹⁶O. S. Oen and D. K. Holmes, *J. Appl. Phys.* 30, 1289 (1959).

THE RANGE OF RADIATION-INDUCED PRIMARY KNOCK-ONS IN THE HARD-CORE APPROXIMATION

D. K. Holmes G. Leibfried¹⁷

The following is an abstract of a paper to be published in the *Journal of Applied Physics*.

The Range of Radiation-Induced Primary Knock-Ons in the Hard-Core Approximation. D. K. Holmes and G. Leibfried. — The slowing down of a primary displaced atom of high energy in a solid is investigated in detail. Physically interesting quantities, such as the total distance traveled and the vector distance to the end of the path, are discussed in terms of certain averages for hard-core potentials with general dependence of the core radius on energy. These averages are explicitly calculated for a screened Coulomb potential for the purpose of comparison with experimental ranges observed in different metals. Theoretical values for the range can be derived. Comparison with the experimental data gives a value for the screening radius of the interaction which is about twice the value originally suggested by Bohr.

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SMALL AMPLITUDE MOTIONS OF DISLOCATION LOOPS

G. Leibfried¹⁸

1. Introduction

It is well known that dislocations in solids contribute to the elastic moduli and to the internal friction.¹⁹ It is generally thought that this is due to the motion of small dislocation loops induced by external stresses. These effects can be suppressed by pinning of the dislocation loops either by impurities¹⁹ or irradiation,²⁰ because by pinning the available loop lengths become smaller, and thus the dislocations cannot move as far as without the pinning. The amplitudes so far used in the experiments are very small, which means that the theoretical treatment can be based on a small amplitude approximation.

The usual theory of these motions starts with the assumption of a line energy. The theoretical treatment is very simple and leads to a differential equation of second order for the amplitudes. Recently, deWit and Koehler²¹ investigated the influence of the dependence of the line energy on the direction of the line, that is, the dependence on edge or screw character of the dislocation loop. The theoretical treatment again is simple. The result can be described by giving an effective line energy which depends on whether the loop is edge or screw type. The results are very interesting and important because the effective line energies can differ very much between edge and screw type loops. Thus, the contribution of loops to the elastic data and internal friction can depend very sensitively on the dislocation character of the loop in question.

It seems worthwhile to investigate the behavior of such loops more closely not assuming the existence of a line energy, because the effective line energies are very sensitive to details and the line energy model is only an approximation. In this more general case, where the elastic field of the dislocation is taken fully into account, the equation for the amplitudes is a complicated integro-differential equation. Solutions can be approximated by using a variational principle. By comparison with the line energy model effective line energies can be calculated. Since all results eventually are always compared with the results of the line energy model, we will present a short review of this model in Sec 2. In Sec 3 the general case will be treated and will be compared with the results of Sec. 2. In the line energy description, two neighbored loops act independent of each other. This is not true for the exact treatment, because these loops interact due to their stress fields. This behavior will be investigated in Sec 4, where it is shown that the loop interaction tends to decrease the effective line energy so as to make pinning somewhat less effective. Finally, in Sec 5 the kinetic energy is discussed. This quantity shows

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¹⁹J. S. Koehler, in *Imperfections in Nearly Perfect Crystals*, p 197, Wiley, New York, 1952.

²⁰D. O. Thompson and D. K. Holmes, *J. Appl. Phys.* 27, 713 (1956); *Phys. and Chem. Solids* 1, 275 (1957).

²¹G. deWit and J. S. Koehler, *The Influence of Elastic Anisotropy on the Dislocation Contribution to the Elastic Constants*, Technical Report No. 5 to the Office of Naval Research, University of Ill., Dept. of Physics, Urbana, May 1958.

only a weak dependence on the character of the dislocation. For the sake of simplicity, only elastically isotropic media are treated.

2. The Line Energy Model

For certain problems in dislocation theory, one can define an energy, E , per unit length of dislocation line. The usual values taken for isotropic materials are

$$E_e = \frac{Gb^2}{4\pi} \frac{1}{1-\nu} \ln \frac{R}{R_c} \quad (1a)$$

for edge dislocations and

$$E_s = \frac{Gb^2}{4\pi} \ln \frac{R}{R_c} \quad (1b)$$

for screw dislocations, where G is the shear modulus, ν is Poisson's ratio, b is the absolute value of the Burgers vector, R_c is an effective core radius (in the order of b), and R is an effective external radius. The value of R depends on the kind of problem.²² For a circular dislocation ring, R is about the radius of the circle; for a random distribution of lines, R can be approximated by the average distance between lines of opposite sign; for a straight line in a finite body, R is in the order of the smallest distance from the line to the surface; etc. Typically, R/R_c is about 10^4 and the logarithm therefore is in the order of 10. Since E is only logarithmically dependent on R/R_c , the exact value of R/R_c is usually thought to be of minor importance.

Equations (1) give essentially the elastic energy. The core energies are given approximately by Eqs. (1) also, if the logarithm is dropped.²³ Thus, in a first approximation the core energy can be included by an appropriate value of R_c .

In the line energy model, a line segment ds of a dislocation line has an energy $E ds$ with²⁴

$$E = E_e \frac{b_{\perp}^2}{b^2} + E_s \frac{b_{\parallel}^2}{b^2} = E_e (1 - \cos^2 \theta) + E_s \cos^2 \theta. \quad (2)$$

Here, $b_{\perp}$ and $b_{\parallel}$ are the components of the Burgers vector $\vec{b}$ perpendicular and parallel to the segment,

²²P. Haasen and G. Leibfried, *Fortschr. Physik* 2, 73 (1955).

²³In the model of Peierls applied to a simple cubic crystal and dislocations with 100 slip planes, exactly these values are obtained for the interaction energy between the two lattice planes which have to be treated atomistically in Peierls' model. The core energy may be slightly larger, since it contains presumably somewhat more than only this plane interaction. Generally, the separation between core and elastic energy is not well defined. Further, it must be kept in mind that in the same case the R_c values for screws and edges are also slightly different. The value for edge dislocations is smaller by a factor $1 - \nu$. These details can and will be changed appreciably for other crystals and other slip systems.

²⁴In isotropic materials, edge and screw dislocations do not interact with each other. Thus, the energy of a straight dislocation line is given by a formula like (2). It is assumed that the same relation holds for small line segments.

and θ is the angle between $\vec{b}$ and $d\vec{s}$ (Fig. 5). An equivalent formulation of (2) is

$$E = E_e (1 - \alpha \cos^2 \theta) , \quad (2a)$$

with

$$\alpha = \frac{E_e - E_s}{E_e} .$$

For isotropy one has $\alpha = \nu$ according to (1). But it can be shown that for dislocations with 110 Burgers vectors in face-centered cubic lattices (2a) can be used as an approximation.^{21,25} In this case the analogs to G and ν in (1) have to be calculated using the anisotropic elastic data of the crystal.

In the line energy model the energies for arbitrary dislocation lines can now be easily calculated. In the following we will always refer to a straight dislocation line along the x axis as the original and stable position. The line motion is governed by the change in energy ϕ caused by deviations from the straight line. The slip plane is taken as the xy plane and the dislocation line is defined by $y = f(x)$ (Fig. 6). Then by using (2a) the following is obtained:

$$\phi = \int dx E_e \left\{ \sqrt{1 + f'^2} [1 - \alpha \cos^2 (\Theta - \Theta')] - (1 - \alpha \cos^2 \Theta) \right\} . \quad (3)$$

Here f' is the derivative of f , $\Theta - \Theta' = \theta$ is the angle between the line segment and Burgers vector, and the meaning of Θ and Θ' is explained in Fig. 6. Introducing $\tan \Theta' = f'$ we obtain

$$\phi = \int dx E_e \left\{ \sqrt{1 + f'^2} \left[1 - \frac{\alpha}{1 + f'^2} (\cos^2 \Theta + 2 \sin \Theta \cos \Theta f' + \sin^2 \Theta f'^2) \right] - (1 - \alpha \cos^2 \Theta) \right\} . \quad (3a)$$

²⁵ A. J. E. Foreman, *Acta Met.* 4, 322 (1955).

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Fig. 5. θ is the Angle Between Burger's Vector $\vec{b}$ and Dislocation Line Element $d\vec{s}$.

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Fig. 6. Arbitrary Dislocation Line $f(x)$ in the xy Slip Plane.

If the interest is only in small deviations $f(x)$ from the original straight line, the integrand of (3a) can be expanded in powers of f keeping only the lowest nonvanishing powers. If one keeps terms up to the second power in f the result is given by

$$\phi = \int dx E_e \left[(1 + \alpha \cos^2 \Theta - 2\alpha \sin^2 \Theta) \frac{f'^2}{2} - 2\alpha \sin \Theta \cos \Theta f' \right] . \quad (3b)$$

If f vanishes in infinity or if, as in loop problems, f vanishes at the boundaries, the term containing f' drops out and one has eventually

$$\phi = \int dx E_{eff} \frac{f'^2}{2} . \quad (4)$$

Here

$$E_{eff} = E_e (1 + \alpha \cos^2 \Theta - 2\alpha \sin^2 \Theta) \quad (5)$$

is an effective line tension which depends on the orientation Θ of the Burgers vector to the original line. The extremal values of E_{eff} are

$$E_{eff} \left(\Theta = \frac{\pi}{2} \right) = E_e (1 - 2\alpha) \quad (5a)$$

for edge dislocations and

$$E_{eff}(\Theta = 0) = E_e (1 + \alpha) \quad (5b)$$

for screw dislocations.

If some points of the dislocation line are pinned on the x axis, one has to require that f vanishes at these points. In the line energy model there is no interaction between different intervals, and each single loop can be treated independently. In the following a loop of length L will be treated. The loop energy ϕ is obtained by (3) or (4) when one confines there the integration to the interval L in question.

If τ is the resolved shear stress in the glide (xy) plane and $\vec{b}$ direction, and if we take τ for the sake of simplicity as constant, then the work done by the external forces ϕ_r is given by

$$\phi_r = \tau b A = \tau b \int_{(L)} f(x) dx , \quad (6)$$

where A denotes the area under the loop. The equilibrium condition for the line segment L can be obtained from a variational principle, namely, that the total energy in the field of the external forces $W = \phi - \phi_r$ be an extremal. The equilibrium condition is then

$$\delta W = \delta(\phi - \phi_r) = 0 , \quad (7)$$

or

$$\delta \int_{(L)} l(f', f) dx = \delta \int_{(L)} \left(E_{eff} \frac{f'^2}{2} - \tau b f \right) dx = 0 . \quad (7a)$$

The variation is here restricted by the usual boundary condition of vanishing variation at the boundaries.

In (7a) the value (4) has been introduced for ϕ , which essentially means small τ . For more general cases one would have to use (3a) instead of (4).

The variational principle (7a) yields the Euler equations

$$\frac{d}{dx} \frac{\partial l}{\partial f'} - \frac{\partial l}{\partial f} = 0, \quad (8)$$

or

$$E_{eff} f'' + \tau b = 0. \quad (8a)$$

The solution of (8a) is a simple parabola. If the loop is taken as symmetrical to $x = 0$ extending from $-L/2$ to $L/2$ (Fig. 7), then

$$f(x) = a \left[1 - \left(\frac{2x}{L} \right)^2 \right], \quad (9)$$

with the maximum amplitude

$$a = \frac{\tau b L^2}{8 E_{eff}}. \quad (9a)$$

The boundary condition $f(\pm L/2) = 0$ is obviously fulfilled. The small amplitude approximation requires $|f'| \ll 1$; the maximum value of the derivative is $4a/L$ at the boundaries of the loop. Therefore, the small amplitude approximation is justified for $4a/L = \tau b L/2 E_{eff} \ll 1$, a condition which usually is met in experiments on dislocation contributions to elastic data and internal friction.

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Fig. 7. Form of a Loop of Length L Under Applied External Stress. The amplitude a is proportional to the stress.

The same result can be obtained if (9) is used as a trial solution and a is determined by minimizing W according to (7). From

$$W = \phi - \phi_r = \frac{8E_{\text{eff}}a^2}{3L} - \frac{2\tau bLa}{3}$$

one gets the minimum value of W for the same value of a as given by (9a).

The contribution of one loop to the resolved elastic shear strain is proportional to the area

$$A = \frac{2La}{3} = \frac{\tau bL^3}{12E_{\text{eff}}}$$

For N such loops per unit volume the dislocation contribution to the shear strain would be NbA . If the loop were pinned in the middle, thus producing two loops $L/2$ out of one loop L , the area of one loop $L/2$ would decrease by a factor of 8 because A is proportional to the third power of the loop length. The total area under the two $L/2$ loops would then be $1/4$ of the area of the L loop. Thus, by decreasing the pinning distance L by a factor of 2 the contribution to the shear strain decreases by a factor of 4. This is roughly the idea used to describe the reduction of the elastic strain by dislocation pinning.

The effective line tension is the essential quantity which determines the amplitude and thereby the dislocation contribution to the elastic behavior. In isotropic materials the two limiting values for E_{eff} are, according to (5), $E_e(1 - 2\nu)$ and $E_e(1 + \nu)$ for edge and screw loops, respectively. The elastic stability²⁶ of the material requires that $-1 < \nu < 1/2$. This results in $E_{\text{eff}}(\Theta) > 0$. Vanishing line energies would occur just for $\nu = 1/2$ and $\nu = -1$. In the first case, E_{eff} would vanish for edge loops, in the second for screw loops. Generally, for $\nu > 0$ edge dislocations have a smaller E_{eff} than screws (here $E_e > E_s$); for $\nu < 0$ this behavior is reversed. Usually one has $\nu > 0$, so that edge dislocations have a larger line energy and edge loops therefore move easier under external stresses. To get an idea of the order of magnitude, let us assume a value of $\nu = 1/3$, which is typical for polycrystalline cubic metals. The ratio of edge to screw amplitudes is given by

$$\frac{a_e}{a_s} = \frac{1 + \alpha}{1 - 2\alpha} = \frac{1 + \nu}{1 - 2\nu}$$

For $\nu = 1/3$, this ratio is 4. deWit and Koehler²¹ have given values for Al ($\alpha = 0.406$), Cu ($\alpha = 0.424$), and Pb ($\alpha = 0.494$), which take into account the elastic anisotropy. The amplitude ratios are then, respectively, 7.5, 9.3, and 114 (!). These values presumably refer to room temperature.

²⁶If the Lamé constants ($H. B. Huntington, Solid State Physics, vol 7, p 214, Academic Press, New York, 1958$), λ and μ , are used, then elastic stability requires for the bulk modulus $\lambda + 2\mu/3 > 0$ and for the shear modulus $\mu > 0$. Poisson's ratio is given by $\nu = \lambda/[2(\lambda + \mu)]$. From the conditions of elastical stability it can now be easily seen that ν is bracketed between -1 and $1/2$. The condition for the bulk modulus yields $-2\mu/3 < \lambda < \infty$ and the corresponding values for ν are $1/2$ for $\lambda = \infty$ and -1 for $\lambda = -2\mu/3$.

High values of the amplitude ratio suggest a strong temperature dependence, since if $(1 + \alpha)/(1 - 2\alpha)$ is large already, small changes in α induce large changes of this ratio. Taking the isotropic values for Al, it is indicated that α increases with temperature, which effects an increase of the amplitude ratio.²⁷

These results, first discussed by deWit and Koehler,²¹ are of great importance for the dislocation contribution to the elastic behavior of crystals. Thus, in general, edge loops are of much larger influence to the elastic strain than screws under otherwise equal conditions. This difference must show up even more in internal friction measurements, because the decrement is inversely proportional to the square of E_{eff} (ref 19).

The difference between edge and screw loops is presumably much more pronounced in small amplitude oscillations than in large amplitude problems. As an example, one can calculate the critical shear stress τ_c for a loop to act as a Frank-Read source. To give an idea of the magnitude of τ_c the variational properties of the problem can be used, because an exact solution may be difficult. If one uses a symmetrical triangular trial solution of amplitude a for which $|f'| = 2a/L$, then the calculation is easy. $W(a)$ can be calculated using (3) and (6). In this case the critical value τ_c corresponds to $a = \infty$ and for $\tau > \tau_c$ a stable equilibrium cannot be maintained. The result is for edge loops

$$\tau_c \left(\Theta = \frac{\pi}{2} \right) = \frac{4bE_s}{L} ,$$

and for screws

$$\tau_c (\Theta = 0) = \frac{4bE_e}{L} .$$

The result is physically obvious, because for edge loops new segments of screw type have to be created, and vice versa. This result shows that there are no singularities to be expected for τ_c . Of course, this calculation is not exact. For example, the exact value for $\alpha = 0$ ($E_s = E_e$) would be $\tau_c = 2bE_e/L$. But, for the ratios, the result should be approximately valid.

In the pinning effects introduced by neutron irradiation, the dependence of E_{eff} on orientation can be rather essential. To indicate the order of magnitude involved, it will be assumed that the distribution of Θ is random and that pinning and friction are independent of Θ . Then the previous theories with angular independent line tension E can be used where E is defined by an appropriate average over the angles. Consequently, one gets for the modulus:

$$\frac{1}{E_M} = \frac{1}{E_{\text{eff}}} = \int_0^{2\pi} \frac{d\Theta}{2\pi E_{\text{eff}}(\Theta)} = \frac{1}{E_e [(1 + \alpha)(1 - 2\alpha)]^{1/2}} \quad (\simeq 2/E_e \text{ for Cu}) ,$$

²⁷Aluminum is not far from isotropy. If one takes for $\nu \simeq C_{12}/(C_{11} + C_{12})$ where C_{11} and C_{12} are the elastic moduli in Voigt's notation (H. B. Huntington, *Solid State Physics*, vol 7, p 214, Academic Press, New York, 1958), then ν changes from 0.363 at absolute zero to 0.385 at 800°K, and the amplitude ratio changes from about 5 to 6.1. The above relation for ν would only be exact for isotropy. These numbers have been given to get an idea what changes are to be expected. For lead, the changes are expected to be much larger.

and for the internal friction

$$\frac{1}{E_{\Delta}^2} = \frac{1}{E_{eff}^2} = \frac{2 - \alpha}{2E_e^2[(1 + \alpha)(1 - 2\alpha)]^{3/2}} \quad (\approx 7.5/E_e^2 \text{ for Cu})$$

This means that different average line tensions are found for the two effects (for Cu with $\alpha = 0.424$: $E_M = E_e/2$ and $E_{\Delta} = E_e/2.74$). These values give only an order of magnitude. For more realistic calculations one has to take into regard the distribution of Θ , which may not be constant, and the dependence of the number of pinning points per unit length on Θ , the character of the dislocation (which presumably is a more important effect), and further, a possible dependence of friction on Θ .

These results of Koehler and deWit show a large sensitivity on the orientation dependence of the line energy. Now the line energy model is an approximation. It is not even known whether the use of the same value of R_c for both edges and screws is justified. As a matter of fact, calculations using the Peierls model show that R_c depends on the character of the dislocation line. Now, near the instability region, where E_{eff} is small, slight changes in the values given in (1) can result in a large effect. It may even be possible that E_e is somewhat larger than the value in (1) and that, therefore, an edge loop can be unstable for values of ν compatible with the elastic stability of the crystal. Further, one knows that, so to say, small pieces of dislocation lines interact by a $1/\text{distance}$ law, and thus one can wonder whether a line energy model with sharply localized energy may be valid at all. Consequently, it seems worth while to investigate the question of loop energies more in detail and to see to what degree of accuracy the line energy approximation is expected to hold. This will be done in the following section.

3. The Elastic Energy

In the following only elastically isotropic media will be treated. For this case Stroh²⁸ has derived a formula for the energy ϕ' of a dislocation line in a glide plane (xy plane) containing the Burgers vector $\vec{b}$:

$$\phi' = \frac{gb^2}{8\pi} \iint \frac{d\vec{s} \cdot A d\vec{\sigma}}{r} \quad (10)$$

This integral is a double line integral. The symbol r stands for the distance between two points (x, y) and (ξ, η) on the dislocation line. The quantities $d\vec{s} = (dx, dy)$ and $d\vec{\sigma} = (d\xi, d\eta)$ are infinitesimal vectors parallel to the line in (x, y) and (ξ, η) , respectively. The symbol A stands for a symmetrical, two-dimensional tensor of rank 2 which operates on the vector $d\vec{\sigma}$.

Stroh²⁸ has given A for $\vec{b}$ parallel to the x axis:

$$A = \begin{Bmatrix} A_{xx} & A_{xy} \\ A_{yx} & A_{yy} \end{Bmatrix} = \frac{1}{1 - \nu} \begin{Bmatrix} 1 - \nu & 0 \\ 0 & 1 \end{Bmatrix} \quad (11)$$

²⁸A. N. Stroh, *Proc. Phys. Soc. (London)* B67, 427 (1954).

It is easy to give the general expression for arbitrary $\vec{b}$ at angle Θ to the x axis,

$$A = \frac{1}{1-\nu} \begin{Bmatrix} 1 - \nu \cos^2 \Theta & -\nu \sin \Theta \cos \Theta \\ -\nu \sin \Theta \cos \Theta & 1 - \nu \sin^2 \Theta \end{Bmatrix} , \quad (11a)$$

which is obtained by using a rotated coordinate system in evaluating (10).

The integral (10) would diverge logarithmically for small distances r . Within the framework of elastic theory a cutoff radius R_c , the "core radius," has to be introduced,²⁹ which means that the integration in (10) is subject to the condition $r \geq R_c$. This condition is taken care of by multiplying the integrand of (10) with a cutoff function $C(r^2 - R_c^2)$:

$$C(\eta) = \begin{cases} 1 & \text{for } \eta \geq 0 \\ 0 & \text{for } \eta \leq 0 \end{cases} .$$

This gives

$$\phi' = \frac{Gb^2}{8\pi} \iint \frac{\sum_{i,k=x,y} A_{ik} ds_i d\sigma_k}{r} C \quad (10a)$$

The dislocation again will be given as in Fig. 6 by $f(x)$. Then $f'(x) dx$ and $f'(\xi) d\xi$ can be substituted in (10a) for dy and $d\eta$, and the following is obtained:

$$\phi' = \frac{Gb^2}{8\pi} \iint dx d\xi \frac{A_{xx} + A_{xy}[f'(x) + f'(\xi)] + A_{yy}f'(x)f'(\xi)}{\{(x - \xi)^2 + [f(x) - f(\xi)]^2\}^{1/2}} C \left\{ (x - \xi)^2 + [f(x) - f(\xi)]^2 - R_c^2 \right\} . \quad (10b)$$

This expression can be expanded in powers of f . If all powers higher than the second are neglected, the result for the energy change is given by

$$\begin{aligned} \phi = \frac{Gb^2}{8\pi} \iint \frac{dx d\xi}{|x - \xi|} & \left(A_{xx}[f(x) - f(\xi)]^2 \left\{ \delta \left[(x - \xi)^2 - R_c^2 \right] - \frac{C}{2(x - \xi)^2} \right\} + \right. \\ & \left. + A_{xy}[f'(x) + f'(\xi)] C + A_{yy}f'(x)f'(\xi) C \right) . \quad (12) \end{aligned}$$

The δ function stems from the expansion of C because $C'(\eta) = \delta(\eta)$. The other terms are obvious. The argument of C has not been written out explicitly; it is naturally $(x - \xi)^2 - R_c^2$, which means that the integration is limited now by $|x - \xi| \geq R_c$.

The A_{xy} term can be dropped. Mathematically, this means that, for example, $f d\xi/|x - \xi|$ should not depend on x ; then $\int f'(x) dx$ gives zero for f vanishing in infinity. For a straight dislocation line in an

²⁹For the lack of better information, R_c is assumed to be constant. There exist other procedures to calculate dislocation energies which correspond to slight changes in the cutoff rules for $r \cong R_c$. But these changes do not give important deviations from the procedure assumed h.e.e.

infinite crystal this term can really be neglected, though the integral diverges logarithmically. This can also be expressed by saying that a straight line should be in (stable or unstable) equilibrium, which requires the vanishing of terms linear in f . Altogether, one has then for small amplitudes

$$\phi = \frac{Gb^2}{8\pi} \iint_{-\infty}^{\infty} dx d\xi \left(A_{xx} [f(x) - f(\xi)]^2 \left\{ \frac{\delta [(x - \xi)^2 - R_c^2]}{R_c} - \frac{C}{|x - \xi|^3} \right\} + A_{yy} \frac{f'(x) f'(\xi)}{|x - \xi|} C \right) . \quad (12a)$$

Even if f is confined to an interval L as discussed in Sec 2, ϕ contains contributions from outside the loop (e.g., $|x| \leq L/2$ and $|\xi| \geq L/2$), showing sort of an interaction of the loop with the rest of the line. Also there would be an interaction between two loops, which simply is an expression of the fact that the energy is not as concentrated as the line energy model assumes.

Nevertheless, the result (12a) has a close resemblance to the line energy picture. Suppose that the δ term can be dropped and that $f(\xi)$ can be replaced by $f(x) + f'(x)(\xi - x)$ in the A_{xx} term and $f'(\xi)$ by $f'(x)$ in the A_{yy} term on account of the denominators, and if the integration can be confined to one loop interval L , then the result is

$$\phi \simeq \frac{Gb^2}{8\pi} \int_{-L/2}^{L/2} dx (2A_{yy} - A_{xx}) \frac{f'(x)^2}{2} \int_{-L/2}^{L/2} \frac{d\xi}{|x - \xi|} C .$$

If the logarithmical dependence on x is neglected in the integral over ξ ,

$$\int_{-L/2}^{L/2} \frac{d\xi}{|x - \xi|} C = \ln \frac{[(L/2) - x][(L/2) + x]}{R_c^2} \simeq 2 \ln \frac{L}{2R_c} ,$$

then ϕ has exactly the same form as in (4), with

$$E_{\text{eff}} = \frac{Gb^2}{4\pi} \ln \frac{L}{2R_c} \frac{1}{1 - \nu} (1 + \nu \cos^2 \Theta - 2\nu \sin^2 \Theta) ,$$

using the values (11a). The agreement with the line energy model (Eqs. 5 and 1a) is complete if the value $L/2$ is chosen for the external effective radius R of Eqs. (1).

4. The Effective Line Energy for One Loop

For an exact treatment one would have to derive an equation for $f(x)$ by means of the variational principle (7). The resulting equation would be a quite complicated integro-differential equation. Rather than make an attempt at solving this equation, we will try to make use of (7) directly. For this purpose a trial solution of the form (9) is assumed and the value of a is determined by variation. Then ϕ_τ is given according to Sec 2 by $2\tau bLa/3$, and ϕ has to be calculated by inserting (9) into (12a). Because there is an interaction over a distance, we have to make an assumption about f outside the loop. We assume vanishing f outside, which means a straight line outside the loop interval.

A comparison with the results of the line energy model of Sec 2 is presumably best made by giving an apparent effective line energy. This is done by comparing the result

$$\phi = \frac{8E_{\text{eff}}a^2}{3L} \quad (13)$$

of Sec 2 with the value calculated by (12a) and (9). If it is not desired to use a solution of the same form as in the line energy model, one better gives an equivalent definition of an apparent line energy, namely, by comparing the loop areas A for given τ and L : $E_{\text{eff}} = \tau b L^3 / 12A$.

The apparent effective line tension defined this way is an upper limit, as can be seen from the variational principle. In other words, the contribution to the elastic strain by trial solutions is always an underestimate. This can be seen in the following way. Since ϕ is quadratic and ϕ_τ is linear in f , the equilibrium value of W is either $-\phi$ or $-\phi_\tau/2$. For the exact solution the value of W is negative and lower than that for trial solutions. Consequently, the approximate value of ϕ or the area is smaller than the correct one.

To ϕ there will be two contributions:

$$\phi = \phi_l + \phi_{l0} \quad (14)$$

Here ϕ_l means loop energy and contains that part of the integral (12a) where x and ξ both are in the loop interval ($|x|, |\xi| \leq L/2$). The term ϕ_{l0} is kind of an interaction with the rest of the line ($|x| \leq L/2, |\xi| \geq L/2$ and $|x| \geq L/2, |\xi| \leq L/2$). The integrations are elementary and give the result:

$$\phi_l = \frac{4Gb^2}{3\pi L} a^2 \left[\frac{A_{xx}}{2} \left(1 - \ln \frac{L}{R_c} + \frac{11}{6} \right) + A_{yy} \left(\ln \frac{L}{R_c} - \frac{7}{3} \right) \right] \quad (15a)$$

$$\phi_{l0} = -\frac{4Gb^2}{3\pi L} a^2 \frac{A_{xx}}{2} \quad (15b)$$

$$\phi = \frac{4Gb^2}{3\pi L} a^2 \left[A_{yy} \left(\ln \frac{L}{R_c} - \frac{7}{3} \right) - \frac{A_{xx}}{2} \ln \left(\frac{L}{R_c} - \frac{11}{6} \right) \right] \quad (15c)$$

The expressions occurring in (14) contain powers of R_c/L . These terms have been neglected because only cases where $L \gg R_c$ (typically $L \cong 10^4 R_c$) will be investigated. The neglected terms play a role only for $L \lesssim 100R_c$. The errors are in the order of R_c/L ; for example, the correct factor of A_{yy} would be

$$\ln \frac{L}{R_c} - \frac{7}{3} + \frac{3R_c}{L} - \frac{2R_c^2}{3L^2} \quad ,$$

where obviously the R_c terms can be dropped for $R_c/L \cong 10^4$. If one neglects such terms, the δ function in (12a) contributes only to ϕ_l [note that $\{f(x) - f(\xi)\}^2 \delta \Rightarrow f'(x)^2 R_c^2 \delta$] in a form as in the line energy model. This yields the 1 in the factor of A_{xx} in (15a).

By comparison with (13) the following is obtained:

$$E_{\text{eff}} = \frac{Gb^2}{4\pi} \left[2A_{yy} \left(\ln \frac{L}{R_c} - \frac{7}{3} \right) - A_{xx} \left(\ln \frac{L}{R_c} - \frac{11}{6} \right) \right] . \quad (16)$$

With respect to this result it is necessary to make some remarks. First of all, it is obvious that for large $\ln L/R_c$ one gets exactly the line energy model taking R in (1) as L . But there are deviations coming about by the fact that the factors of $2A_{yy}$ and A_{xx} are not quite equal. If the factors were equal, one again would get the line energy description by redefining R or R_c . Equation (16) has quite inconvenient properties from the point of view of stability. If we write (16) in the following way:

$$E_{\text{eff}} = \frac{Gb^2}{4\pi} \left[(2A_{yy} - A_{xx}) \ln \frac{L}{R_c} e^{7/3} - \frac{A_{xx}}{2} \right] , \quad (16a)$$

it is seen that E_{eff} becomes zero if

$$\ln \frac{L}{R_c} e^{7/3} \leq \frac{A_{xx}/2}{2A_{yy} - A_{xx}} .$$

Or, in other words, the line becomes unstable if L is smaller than the value given by the equality sign. (This instability may be connected with the general instabilities for distribution of singularities of linear field equations.) This value may well be within the range of the validity of these formulas, particularly if $2A_{yy} - A_{xx}$ is very small ($\nu \lesssim 1/2$ or $\nu \gtrsim -1$), and the loop would be very nearly unstable in the line energy picture. This value of L can be absolutely large, which means that the formulas apply.

On the other hand, the assumption of keeping the line straight outside the loop is physically not very sensible. It can be easily seen that the interaction ϕ_{l0} between the loop and the rest of the line is rather important for the stability. If ϕ_{l0} is neglected, then the last term $-A_{xx}/2$ in (16a) would change in sign to $+A_{xx}/2$. Then E_{eff} would never go to zero, and just in the instability region where $2A_{yy} - A_{xx}$ is small there would be large differences in comparison to the line energy model. This shows that the course of the line near the loop may play an important role for the numerical value of E_{eff} if the logarithmic term is small.

Taking into regard a genuine core energy would also influence the result. If an orientation-independent core energy $E_c = (Gb^2/4\pi) \epsilon_c$ is assumed, then the result is

$$E_{\text{eff}} = \frac{Gb^2}{4\pi} \left[(2A_{yy} - A_{xx}) \ln \frac{L}{R_c} e^{7/3} - \frac{A_{xx}}{2} + \epsilon_c \right] . \quad (16b)$$

Values of ϵ_c in the order of 1 to 2 are not unreasonable, and since $A_{xx} = (1 - \nu \cos^2 \Theta)/(1 - \nu)$ is bracketed between $1/2$ and 2, the expression (16b) would always be positive for $\epsilon_c > 1$. The orientation dependence of ϵ_c is not known, nor is there at present sufficient information on how to separate elastic and core energies. This could be done by closer investigation of models (e.g., Peierls' model) for arbitrary dislocation contour where the energies are well defined and a cutoff procedure is not required.

That is, the influence of the lattice structure on the dislocation structure has to be investigated in more detail. Both magnitude and orientation dependence of ϵ_c are very important here. In extended dislocations, as is the case in copper, the orientation behavior of the extension would also have to be considered.

It may be mentioned that other choices of the cutoff procedure do not change the qualitative behavior of E_{eff} . Small changes of this procedure for distances $r \sim R_c$ always give contributions of the same form as the line energy model. Thus, the only change is in the numerical factor of $2A_{yy} - A_{xx}$ in (16) – not the qualitative behavior. For instance, if C/r in (10a) is replaced by $C/r + (1 - C)/R_c$, which means that for $r < R_c$ there is a constant value $1/R_c$ in the integrand rather than zero assumed in the cutoff (10a), then this only replaces the factor $e^{7/3}$ in (16b) by $e^{4/3}$.

The whole purpose of this discussion is to show that for small E_{eff} the values given by the line energy model are not dependable, because then all the other unknown effects play an important role. If, as an example, the case $\nu \cong \frac{1}{2}$ is treated, and if the logarithm in (16b) is of the order of 10, then the bracket in (16b) is about 30 for screw loops and $\epsilon_c - 1$ for edge loops. For screw loops the logarithmic term is large; for edge loops it vanishes. In the latter case the core energy and other small influences determine E_{eff} . Consequently, just in the interesting case of small line energies, according to the line energy description, the value of E_{eff} is undependable. If the core energy were given by $\epsilon_c \cong 2$, this would give an upper limit of $a_e/a_s \cong 30$. The general trend of the line energy picture is kept, but quantitative data can only be obtained by properly taking into regard the core energy.

As discussed above, the interaction of the loop with the rest of the line can be quite important for small E_{eff} . Therefore, deviations which are due to the course of the rest of the line must be expected. Usually one has not to do with straight lines, but the lines will show kinks at the natural pinning points in the dislocation network, with the effect that the starting configuration would not be a straight line, not to speak of the internal stresses effected by the whole network. Then it should be kept in mind that the calculated E_{eff} is an underestimate. But it is felt that the deviations due to these influences are not really serious. Altogether, the general behavior of the line energy model remains, namely, that edge loops usually have considerably less effective line energy than screw loops (for $\nu > 0$), though the quantitative results are doubtful to some extent.

5. The Interaction Between Two Loops

To decide the question of loop interaction we consider the same L interval as before but introduce a new pinning point at $x = 0$ (Fig. 8). In the line energy model the two loops $(-L/2, 0)$ and $(0, L/2)$ are completely independent. As discussed in Sec 2, the contribution to the elastic strain of the two loops decreases by a factor $\frac{1}{4}$ as compared with one loop L under equal external stress.

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Fig. 8. Dislocation Loop with 3 Pinning Points at $x = \pm L/2$ and $x = 0$.

Again the solution of the line energy model,

$$f(x) = \begin{cases} a \frac{8}{L} \left(|x| - \frac{2}{L} x^2 \right) & \text{for } |x| \leq L/2, \\ 0 & \text{for } |x| \geq L/2, \end{cases} \quad (17)$$

is used as a trial solution and the amplitude a is determined by variation. By comparison with the results of the line energy description for this case,

$$\phi = 2 \frac{8E_{eff}}{3L/2} a^2, \quad (18)$$

an effective apparent line energy can again be defined.

By inserting (17) into (12a) one can calculate ϕ , which now contains three terms:

$$\phi = \phi_l + \phi_{l0} + \phi_{ll}. \quad (19)$$

Here ϕ_l is the loop energy, ϕ_{l0} the interaction with the rest of the line, and ϕ_{ll} the interaction between the two loops. Every term corresponds to certain integration limits in (12a).

More specifically, ϕ_l is the contribution from (12a) where x and ξ are both in the same loop interval. Since both loops must give the same contribution, we have

$$\phi_l = 2 \iint_{\substack{0 \leq x \\ \xi \leq L/2}} dx d\xi l, \quad (20)$$

where $l(x, \xi)$ means the integrand in (12a). This integral has been evaluated already in Sec 4. The result is obviously twice the value of (15a) when one substitutes there $L/2$ for L :

$$\phi_l = 2 \frac{4Gb^2}{3\pi L/2} a^2 \left[\frac{A_{xx}}{2} \left(1 - \ln \frac{L}{2R_c} + \frac{11}{6} \right) + A_{yy} \left(\ln \frac{L}{2R_c} - \frac{7}{3} \right) \right]. \quad (20a)$$

Because of the $x\xi$ symmetry of the integrand and the symmetry of $f(x)$ itself, the following is obtained:

$$\phi_{l0} = 4 \iint_{\substack{0 \leq x \leq L/2 \\ \xi \geq L/2}} dx d\xi + 4 \iint_{\substack{0 \leq x \leq L/2 \\ \xi \leq -L/2}} dx d\xi . \quad (21)$$

The second integral can be neglected because it is smaller by about a factor of $1/20$ than the first one. The first integral is just the value of (15b) replacing L by $L/2$:

$$\phi_{l0} = -\frac{4Gb^2}{3\pi L/2} a^2 \frac{A_{xx}}{2} . \quad (21a)$$

The interaction between the two loops is given by

$$\phi_{ll} = 2 \iint_{\substack{0 \leq x \leq L/2 \\ -L/2 \leq \xi \leq 0}} dx d\xi . \quad (22)$$

The result of this integration is

$$\phi_{ll} = -2 \frac{4Gb^2}{3\pi L/2} \left[\frac{A_{xx}}{2} (19 \ln 2 - 13) + A_{yy} (1 - \ln 2) \right] . \quad (22a)$$

The effective line energy for this problem is then obtained by comparing the result for ϕ with (17),

$$E_{\text{eff}} \left(\frac{L}{2} \right) = \frac{Gb^2}{4\pi} \left[2A_{yy} \left(\ln \frac{L}{2R_c} - \frac{7}{3} - 1 + \ln 2 \right) - A_{xx} \left(\ln \frac{L}{2R_c} - \frac{17}{6} + 19 \ln 2 - 13 + \frac{1}{2} \right) \right] , \quad (23a)$$

or

$$E_{\text{eff}} \left(\frac{L}{2} \right) = \frac{Gb^2}{4\pi} \left[2A_{yy} \left(\ln \frac{L}{R_c} - \frac{10}{3} \right) - A_{xx} \left(\ln \frac{L}{R_c} - \frac{17}{6} \right) \right] , \quad (23b)$$

since $18 \ln 2 - 13 \approx -1/2$. Comparing this with (16), it is seen that the effect is just to replace L by L/e . Consequently, when pinning at $x = 0$, one has to deal with a slightly decreased apparent line energy. The decrease is somewhat larger than just the expected replacement of L by $L/2$.

If $E_{\text{eff}}(L/2)$ is written in the form (16a), one has

$$E_{\text{eff}} \left(\frac{L}{2} \right) = \frac{Gb^2}{4\pi} \left[(2A_{yy} - A_{xx}) \ln \frac{L}{R_c} e^{10/3} - \frac{A_{xx}}{2} \right] . \quad (23c)$$

For $\ln L/R_c \approx 10$, the logarithmic term therefore changes by about 15%, which is not very much and may be neglected in a first approximation. Or in other words, the assumption of an essentially L -independent effective line energy is valid approximately, though the pinning is somewhat less effective.

If the sign of one of the loops is reversed, then one has a situation as in the first excited oscillation of the loop. The energy for this state is larger than ϕ according to (19), (20-22) because in this situation the integrals required stay the same except for ϕ_{ll} , which changes its sign. Consequently, the effective

line energy for this oscillation is larger than E_{eff} according to (23b). It rather increases somewhat over the value in (16). But here also this change can approximately be neglected.

This interaction between two loops will also show up in large amplitude problems. A reduction of the critical shear stress as compared with the line energy model for loops with an additional pinning point should be anticipated.

What has been said in the discussion about possible contribution of core energies applies here also and will not be repeated. But it should be remarked that a discussion of (23c) without a core energy would show large variations of E_{eff} passing from one to two loops, if one is near the condition of elastic instability.

Altogether it can be concluded that the line energy model may be used approximately here also, if one does not forget about the limitation of the amplitude ratio or E_{eff} by the influence of the core.

6. Kinetic Energies

For the treatment of dynamic processes the kinetic energy of motion ϕ_{kin} for given $f(x,t)$ is needed. The variational principle is then

$$\delta \int W dt = 0 ,$$

where $W = \phi - \phi_\tau - \phi_{kin}$. In the elastic theory the kinetic energy is given by

$$\phi_{kin} = \int \frac{\rho}{2} \dot{u}^2 dx dy dz , \quad (24)$$

where $u(x,t)$ is the displacement field, $\dot{u}$ its time derivative, and ρ the mass density of the material. The field u has to be calculated for given f and the integration in (24) must then contain a cutoff factor which drops contributions inside a distance R_c of the dislocation line, because u becomes singular in the line itself.³⁰

In this formulation the friction is not contained. This can be added later. The kinetic energy essentially determines the resonance frequency of a loop. In the line energy model the kinetic energy would be defined in the following way:

$$\phi_{kin} = \int \frac{E[f(x,t)]^2}{2C^2} dx , \quad (25)$$

where $Ev^2/2C^2$ is the kinetic energy per unit length of a dislocation line moving with velocity v . Because the kinetic energy is already quadratic in f , the quantities E and C refer to the original straight

³⁰ This cutoff condition is not quite the same as that used in Sec 3. One could use for ϕ the same condition as here, integrating over the energy density, but the previous condition is easier to handle in the calculation of ϕ . Anyhow, one would not expect different cutoff conditions only to give very different results. Whether both the values of R_c are the same will be discussed later.

line. The general expression would depend on Θ only in the form

$$\frac{E}{C^2} = \frac{E_e}{C_e^2} \sin^2 \Theta + \frac{E_s}{C_s^2} \cos^2 \Theta . \quad (25a)$$

The velocities C_s and C_e can be determined by investigating the motion of a straight edge or screw dislocation, and the result is

$$C_s^2 = C_t^2 \quad (26)$$

for screw dislocations,³¹ where C_t is the velocity of sound of transversal waves. For edge dislocations a similar result is obtained:

$$C_e^2 = C_t^2 \frac{4(1-\nu)}{5-12\nu+8\nu^2} . \quad (26a)$$

The equation of motion would be

$$\frac{E \ddot{f}}{C^2} = E_{\text{eff}} f'' - \tau b . \quad (27)$$

Here τ can depend on time. The ground wave for $\tau = 0$ is given by

$$f(x,t) = a(t) \cos \frac{\pi x}{L} ,$$

where $a(t)$ is harmonic according to (27). The frequency ω then is given by

$$\frac{E}{C^2} \omega^2 = E_{\text{eff}} \left(\frac{\pi}{L} \right)^2 ; \quad \omega^2 = \frac{E_{\text{eff}}}{E} \left(\frac{\pi C}{L} \right)^2 . \quad (28)$$

This, then, is the first resonance frequency in the line energy model. In this model E_{eff} can become very small if $\nu \lesssim \frac{1}{2}$, whereas E and C^2 always stay positive. Thus a variation in E_{eff} due to orientation of loops can give considerable spread out of resonance frequencies.

Again this simple determination of the kinetic energy may be doubtful and more refined methods for calculations are needed. If the dislocation line is given by $f(x,t)$ and if f is small, the displacement $\vec{u}(x)$ can be expanded in powers of f :

$$\vec{u} = \vec{u}^{(0)} + \vec{u}^{(1)} + \dots , \quad (29)$$

where $\vec{u}^{(0)}$, the displacement field of the straight line, does not contain f and $\vec{u}^{(1)}$ is proportional to f . Consequently, the result is

$$\dot{\vec{u}} = \dot{\vec{u}}^{(1)} + \dots . \quad (29a)$$

³¹J. D. Eshelby, *Proc. Roy. Soc. (London)* A197, 396 (1949).

Because only terms which are quadratic in f are taken into regard, the kinetic energy is

$$\phi_{kin} = \int \frac{\rho}{2} \left[\dot{u}^{(1)} \right]^2 dx dy dz . \quad (24a)$$

The cutoff condition here refers to the original straight line because taking into regard the condition referring to the real loop would introduce higher than quadratic terms in f .

The displacement field of a dislocation is generally given by³²

$$4\pi \vec{u}(\vec{x}) = \vec{b} \Omega + \vec{b} \times \frac{d\vec{\sigma}}{r} + \frac{1}{2(1-\nu)} \text{grad} \int (\vec{b} \times \vec{r}) \cdot \frac{d\vec{\sigma}}{r} . \quad (30)$$

Here it is: $\vec{r} = \vec{x} - \vec{\xi}$, $d\vec{\sigma} = d\vec{\xi}$, and Ω the solid angle under which the dislocation appears from the point $\vec{x}$. The integrals are line integrals along the dislocation line. The solid angle can also be expressed by a line integral.³² The expansion of $\vec{u}$ can be carried out exactly as in Sec 3. If the Burgers vector $\vec{b} = (b_x, b_y, 0)$ has no z component, the result of this expansion is

$$4\pi u_x^{(1)} = \int d\xi \left\{ -\frac{b_x z f(\xi)}{r^3} + \frac{1}{2(1-\nu)} \frac{\partial}{\partial x} \left[\frac{b_y z y f(\xi)}{r^3} - \frac{b_x z f'}{r} \right] \right\} , \quad (31a)$$

$$4\pi u_y^{(1)} = \int d\xi \left[-\frac{b_y z f}{r^3} + \frac{1}{2(1-\nu)} \frac{\partial}{\partial y} \left(\frac{b_y z y f}{r^3} - \frac{b_x z f'}{r} \right) \right] , \quad (31b)$$

$$4\pi u_z^{(1)} = \int d\xi \left[\left(\frac{b_x f'}{r} - \frac{b_y y f}{r^3} \right) + \frac{1}{2(1-\nu)} \frac{\partial}{\partial z} \left(\frac{b_y z y f}{r^3} - \frac{b_x z f'}{r} \right) \right] . \quad (31c)$$

Here r is $[(x - \xi)^2 + y^2 + z^2]^{1/2}$. The first term in (31a, b) is the expansion of the solid angle, which is quite obvious. The other terms are the expansions of the line integrals occurring in (30). The expressions (31) contain terms proportional to b_x and b_y :

$$4\pi u_x^{(1)} = \int d\xi \left\{ b_x \left[-\frac{z f}{r^3} - \frac{1}{2(1-\nu)} \frac{\partial}{\partial x} \frac{z f'}{r} \right] + b_y \frac{1}{2(1-\nu)} \frac{\partial}{\partial x} \frac{z y f}{r^3} \right\} , \quad (32a)$$

$$4\pi u_y^{(1)} = \int d\xi \left\{ -b_x \frac{1}{2(1-\nu)} \frac{\partial}{\partial y} \frac{z f'}{r} + b_y \left[-\frac{z f}{r^3} + \frac{1}{2(1-\nu)} \frac{\partial}{\partial y} \frac{z y f}{r^3} \right] \right\} , \quad (32b)$$

³²M. Peach and J. S. Koehler, *Phys. Rev.* 80, 436 (1950).

$$4\pi u_z^{(1)} = \int d\xi \left\{ b_x \left[\frac{f'}{r} - \frac{1}{2(1-\nu)} \frac{\partial}{\partial z} \frac{zf'}{r} \right] - b_y \left[\frac{yf}{r^3} - \frac{1}{2(1-\nu)} \frac{\partial}{\partial z} \frac{zyf}{r^3} \right] \right\} . \quad (32c)$$

If we split $f(x,t)$ into a time-dependent amplitude $a(t)$ and an x -dependent shape of the curve $f(x,t) = a(t)G(x)$, then we have $\dot{f} = \dot{a}G = \dot{a}/a$ and also $\dot{f}' = \dot{a}f'/a$. Therefore it is

$$\phi_{\text{kin}} = \frac{\dot{a}^2}{a^2} \int \frac{\rho}{2} \vec{u}^{(1)2} dx dy dz , \quad (33)$$

where the integration is limited by $y^2 + z^2 \geq R_c^2$. It is now easy to see that in ϕ_{kin} the terms containing b_x and b_y are separated. Or, in other words, the kinetic energy

$$\phi_{\text{kin}} = \frac{b_x^2}{b^2} \phi_{s,\text{kin}} + \frac{b_y^2}{b^2} \phi_{e,\text{kin}} \quad (33a)$$

is separated in independent screw and edge contributions, which is analogous to Eq. (2) referring to the separations of line energies. Use of this separation has already been made in (25a). This separation is due to the fact that the b_x and b_y terms have different symmetry with respect to rotations around the x axis; for example, in (32a) the b_x term is proportional to z and the b_y term to zy . Mixed terms in (33) would be proportional to z^2y and would not contribute to (33).

It does not at first seem that the results (25) and (26) will hold, because evidently $\phi_{s,\text{kin}}$ contains ν , whereas E_s/C_s^2 in (25) according to (26) does not. This alone suggests a closer investigation of ϕ_{kin} .

The displacement $\vec{u}^{(1)}$ is the displacement field of a small dislocation ring along the loop and the x axis taking only first powers of f into account. The sign of the expression can be checked because $\vec{u}^{(1)}$ must be a solution of the elastic equations.

It must be kept in mind that this calculation, as well as the whole concept of kinetic energy, is only valid for velocities small as compared with the characteristic velocities of sound. In all oscillation measurements carried out so far this condition is well satisfied.

To avoid divergence difficulties one can replace f' by $f' \partial/\partial x$ by partial integration. Then $\vec{u}^{(1)}$ is expressed by $f(\xi)$ alone:

$$4\pi u_x^{(1)} = \int f(\xi) d\xi \left[-b_x \left(\frac{z}{r^3} + \gamma \frac{\partial^2}{\partial x^2} \frac{z}{r} \right) + b_y \gamma \frac{\partial}{\partial x} \frac{zy}{r^3} \right] , \quad (34a)$$

$$4\pi u_y^{(1)} = \int f(\xi) d\xi \left[-b_x \gamma \frac{\partial^2}{\partial y \partial x} \frac{z}{r} - b_y \left(\frac{z}{r^3} - \gamma \frac{\partial}{\partial y} \frac{zy}{r^3} \right) \right] , \quad (34b)$$

$$4\pi u_z^{(1)} = \int f(\xi) d\xi \left[b_x \left(\frac{\partial}{\partial x} \frac{1}{r} - \gamma \frac{\partial^2}{\partial z \partial x} \frac{z}{r} \right) - b_y \left(\frac{y}{r^3} - \gamma \frac{\partial}{\partial z} \frac{zy}{r^3} \right) \right] , \quad (34c)$$

where $\gamma = 1/[2(1 - \nu)]$. Then the kinetic energy can be written as a double integral over ξ and ξ' for example,³³

$$\phi_{s,kin} = \frac{\rho b_x^2}{2(4\pi)^2} \iint d\xi d\xi' f(\xi) f(\xi') F_s(\xi, \xi') \frac{\dot{a}^2}{a^2}, \quad (35)$$

where $F(\xi, \xi')$ has the dimension of a reciprocal length. Furthermore, it can be easily seen that F depends only on the absolute value of $\xi - \xi'$: $F(|\xi - \xi'|) = F(|\Delta|)$, with $\Delta = \xi - \xi'$. For $\Delta \neq 0$ the corresponding integrals converge without any cutoff condition; here F_s presumably has the form

$$F_s(\Delta) = \bar{F}_s \frac{1}{|\Delta|},$$

which is analogous to the expressions occurring in ϕ . Therefore F_s and F_e will be calculated for $\Delta \neq 0$ and the cutoff condition will be replaced by $|\Delta| \geq R_c$ as in Sec 3, where now both R_c have the same meaning. This procedure is chosen because the integrations are becoming too complicated. The general trend, however, is not changed by using another cutoff condition.

The integrations can easily³⁴ be carried out, and the results are, for screw dislocations,

$$F_s(\Delta) = \frac{2\pi}{|\Delta|}, \quad (35a)$$

and for edge dislocations,

$$F_s(\Delta) = \frac{2\pi}{|\Delta|} (2 - 2\gamma + \gamma^2) = \frac{2\pi}{|\Delta|} \frac{5 - 12\nu + 8\nu^2}{4(1 - \nu)^2}. \quad (35b)$$

Here again, terms proportional to R_c have been omitted. Thus the ratio of kinetic energies for screw and edge dislocations is the same as one would get for the motion of straight lines. This ratio does not depend very much on ν . The factor in (35b) has a minimum at $\nu = 1/2$ with the value 1. For $\nu = 0$ it would be $5/4$, and for the other extreme case at $\nu = -1$ it is $25/16$. Consequently, the variance of resonance frequencies with orientation of loops is essentially due to the effective line energy.

This result can be used to derive a dependable value for the kinetic energy. As earlier, we use Eq. (9) with time-dependent amplitude to describe the loop motion. Then the following is obtained approximately:

$$\phi_{s,kin} \approx \dot{a}^2 \frac{\rho b^2}{16\pi} L \ln \frac{L}{R_c e} \quad (36a)$$

³³ In (35), $f(\xi) f(\xi') \dot{a}^2/a^2$ can as well be replaced generally by $\dot{j}(\xi, t) \dot{j}(\xi', t)$.

³⁴ The integrations are most easily done by using the Fourier transform of $1/r = \int d\vec{k} e^{i\vec{k} \cdot \vec{x}} / 2\pi^2 k^2$ and of $z/r = -\int d\vec{k} e^{i\vec{k} \cdot \vec{x}} / ik_z \pi^2 k^4$.

and

$$\phi_{e, \text{kin}} \approx \dot{a}^2 \frac{\rho b^2}{16\pi} L \frac{5 - 12\nu + 8\nu^2}{4(1 - \nu)^2} \ln \frac{L}{R_c e} . \quad (36b)$$

Again, terms proportional to R_c have been omitted. Further, the exact result would contain factors which differ from (36) only by some per cent, which is spurious for the present application.

If the same solution is used in (25), the result is

$$\phi_{\text{kin}} = \frac{\dot{a}^2 E}{3C^2} L . \quad (37)$$

By comparison with (36) one obtains the value of E/C^2 , which can be used for determining the resonance frequencies according to (28). Since $\rho = G/C_t^2$, one can write (36a) as

$$\phi_{s, \text{kin}} \approx \dot{a}^2 \frac{Gb^2}{4\pi} \frac{L}{4C_t^2} \ln \frac{L}{R_c e} . \quad (36a')$$

By comparison with (25a) it is seen that the value of E_s in the kinetic energy for screw dislocations, taking $C_s = C_t$,

$$E_s \approx \frac{Gb^2}{4\pi} \frac{3}{4} \ln \frac{L}{R_c e} ,$$

is typically of the order of usual line energies. For edge dislocations, a slightly different, ν -dependent, result is obtained. The value of E/C^2 for either case is about the same, which shows that a variance in the resonance frequencies is practically due only to changes in E_{eff} .

For $\nu = 0$, screws and edges are energetically equivalent, but the kinetic behavior is nevertheless different. The reason for this is that they introduce quite different kinds of elastic fields containing different amounts of longitudinal and transversal fields. And longitudinal velocities deviate from transversal velocities in the whole stability range of elastic data.

7. Conclusions

The kinetic energy for motions of dislocation loops is a relatively well-defined quantity within the frame of elastic theory of dislocations. The potential energy, however, is sensitive to the behavior of the core and the vicinity of the loop in question. For small energetic differences between edge and screw dislocations ($\nu \approx 0$) in isotropic materials, it is shown that the line energy model is correct. For large differences ($\nu \lesssim 1/2$; $\nu \gtrsim -1$) the core behavior can be essential and determine the effective line energy. A more thorough investigation, taking into regard the details of the core structure, would be very valuable.

STUDIES ON THE STRUCTURE OF RADIATION-INDUCED DISPLACEMENT CASCADES

G. Leibfried³⁵

Introduction

In the irradiation of solids with high-energy particles the main contribution to structural damage is caused by collisions with the atoms of the solid. Primary knock-ons of sufficient energy can leave their lattice sites and eventually produce a cascade of interstitials and vacancies by subsequent collisions with other atoms of the lattice. The number of defects contained in a cascade should be roughly proportional to the primary energy. The spectral distribution of primary energies depends on the kind of radiation. Generally, the average energy transfer is much larger for neutron irradiation than for charged-particle irradiation. Consequently, for neutron irradiation the investigation of the structure of cascades effected by high-energy primaries is of particular interest.

For a theoretical treatment of the atomic collisions it is necessary to start with the repulsive interaction potential between the atoms of the solid. The theory of these interaction potentials is extremely complicated and the present state of theory does not allow the derivation of a dependable potential. But if a reasonable form for the potential is assumed, the parameters involved can be determined by comparison with experimental data. In metals, for "low" energies a Born-Mayer potential is generally assumed which depends exponentially on the distance and describes essentially the atomic core repulsion due to exchange forces. The parameters can be determined by comparison with the elastic data.³⁶ Further, other low-energy phenomena, such as the Wigner energy of the crystal, can be used to adapt the potential values.^{36,37} For "high" energies Bohr³⁸ has suggested a screened Coulomb potential which particularly describes the Coulomb interaction between nuclear charges screened by the surrounding electrons. The screening radius can be determined by using recent experimental values^{39,40} of primary ranges in metals. In this way expressions for the potential in the high- and low-energy region can be obtained.

In the following the discussion will essentially refer to copper, though the general treatment also would apply to other metals, because for copper the experimental data on the potential are most dependable. Here the limit between "low" and "high" energies should be on the order of 1000 ev. ("Low" energies refer to distances on the order of atomic distances, "high" energies to distances of the order of the screening radius which for Cu is about one-tenth of the atomic distance.) Fortunately the low- and the high-energy expressions for the interaction potential in copper do not perturb each other, which means that in the low-energy region the Bohr potential is small compared with the Born-Mayer potential and

³⁵On leave from Technische Hochschule, Aachen, Germany.

³⁶H. B. Huntington, *Phys. Rev.* **93**, 1414 (1954).

³⁷G. Leibfried, *J. Appl. Phys.* **30**, 1388 (1959).

³⁸N. Bohr, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **18**, No. 8 (1948).

³⁹R. A. Schmitt and R. A. Sharp, *Phys. Rev. Letters* **1**, 445 (1958).

⁴⁰D. K. Holmes and G. Leibfried, *J. Appl. Phys.* (to be published). See abstract, "The Range of Radiation-Induced Primary Knock-Ons in the Hard-Core Approximation," this report.

vice versa. Thus in this case the sum of both potentials can be used as a reasonable expression for the whole energy region, which fits the experimental data at both sides well.

In the energy range of interest here the atomic collisions can be treated as hard-core collisions with energy-dependent hard-core radius. For hard-core collisions averages can be calculated⁴⁰ which give an idea of the interstitial distribution and the size of a cascade. The expressions for these averages could be evaluated numerically. Instead of this, approximate expressions, accurate to about 30%, are used since the uncertainty in the potential values does not seem to justify a numerical evaluation.

The results are discussed particularly with respect to copper. It is shown that the density of defects in the cascade depends on the primary energy, showing a maximum density of about 5 at. % for primary energies of about 1000 ev.

Averages in the Hard-Core Approximation

If a primary knock-on is produced by irradiation, it is slowed down by collisions with other atoms of the lattice. Figure 9 shows the collision history of the primary. It starts in direction $\vec{u}_0$ with energy E_0 . At the first collision point (1) after having traversed the distance l_0 , direction and energy are changed to $\vec{u}_1$ and E_1 . Out of this collision a secondary knock-on with $\vec{u}_1'$ and E_1' emerges. The distribution of directions, energies, and collision points depends on the interaction potential. If the energy left after the first collision is larger than the displacement energy E_d of the solid, the primary can travel further and displace other atoms by subsequent collisions; the same holds true for the secondary knock-ons. In this way a cascade of interstitials and vacancies can be produced. The number of interstitials and

Fig. 9. Collision Series of a Primary Knock-On Starting at (0). The broken lines denote secondary and tertiary knock-ons.

vacancies ν contained in a cascade is about^{41,42}

$$\nu(E_0) = \frac{E_0}{2E_d} \quad \text{for } E_0 > 2E_d. \quad (1)$$

This is an average value, but it can be shown⁴³ that the variance of ν is small for large ν . Thus the number of defects in a cascade is in general a well-defined value. A typical value for E_d in most metals is about 25 ev.

To get an idea of the spatial structure of the cascade, the collision history of the primary knock-on as well as that of the secondary, tertiary, etc., knock-ons has to be investigated in more detail. It would be most valuable to calculate the whole distribution function $W(\vec{r}_1, \dots, \vec{r}_\nu) d\vec{r}_1 \dots d\vec{r}_\nu$, which means the probability for finding the eventual positions $\vec{r}_1, \dots, \vec{r}_\nu$ of the ν interstitials in the respective intervals. This is much too complicated, however, and we must be content to calculate averages over the distribution function, which already give an idea of the size and the structure of the cascade.

If the potential of two atoms at distance r is $\phi(r)$, the distance of closest approach R is related to the collision energy E by

$$\phi(R) = \frac{E}{2}. \quad (2)$$

Generally, one has to use in (2) the energy of relative motion for the two colliding atoms in question. But because we deal only with collision processes between equal partners where one atom has the energy E and the other is at rest, the energy of relative motion is given by $E/2$.

In the energy range of interest here the potential falls off with distance so rapidly that the collision can be described as a collision between two hard cores. That is, the potential can be replaced by a hard-core potential with energy-dependent core radius $R(E)$ given by (2). This replacement of ϕ by a hard-core potential simplifies the treatment very much because hard-core scattering has very simple and symmetric properties. Let us, for instance, investigate the first collision in Fig. 9 more in detail. The scattering law determines the distribution of the quantities $\vec{u}_1, E_1, \vec{u}_1', E_1'$ after the first hit. These quantities are correlated by conservation of momentum and energy

$$\vec{u}_0 \cdot \vec{u}_1 = \left(\frac{E_1}{E_0} \right)^{1/2},$$

$$\vec{u}_1 \cdot \vec{u}_1' = 0,$$

$$E_1 + E_1' = E_0,$$

⁴¹G. H. Kinchin and R. S. Pease, *J. Nuclear Energy* 1, 200 (1955).

⁴²F. Seitz and J. S. Koehler, *Solid State Physics*, vol 2, p 305, Academic Press, New York, 1956.

⁴³G. Leibfried, *Nukleonik* 1, 57 (1958).

but the distribution itself is completely symmetric with respect to interchanging the quantities referring to the primary and the secondary knock-on. The probability for finding the energies in the intervals (E_1, dE_1) and (E'_1, dE'_1) and the directions in the solid angle elements $d\Omega_1, d\Omega'_1$ would be⁴⁰

$$\delta\left(\vec{u}_1 \sqrt{\frac{E_1}{E_0}} + \vec{u}'_1 \sqrt{\frac{E'_1}{E_0}} - \vec{u}_0\right) \delta(E_1 + E'_1 - E_0) \sqrt{E_1 E'_1} \frac{dE_1 d\Omega_1 dE'_1 d\Omega'_1}{8\pi E_0^2},$$

$$\delta\left(\vec{u}_1 \cdot \vec{u}_0 - \sqrt{\frac{E_1}{E_0}}\right) \frac{dE_1 d\Omega_1}{2\pi E_0}$$

for one particle alone. This shows that the distribution $w(\vec{r}) d\vec{r}$ of the eventual position of the primary and the distribution $w(\vec{r}') d\vec{r}'$ of the secondary are exactly the same. The distribution w can be obtained by integrating the complete distribution W over all coordinates except the one of interest. The same reasoning can be applied to any interstitial produced. Consequently, the distribution for any interstitial is the same. It has been shown⁴⁰ that averages over the distribution $w(\vec{r})$ can be easily calculated for arbitrary energy dependence of the hard-core radius. Particularly, expressions for the following averages have been given:

$$\bar{x} = \lambda(E_0) + \int_0^{E_0} \lambda(\epsilon) \frac{d\epsilon}{\sqrt{\epsilon E_0}}, \quad (3)$$

$$\frac{\overline{r^2}}{2} = \lambda^2(E_0) + \int_0^{E_0} \left[\frac{\lambda^2(\epsilon)}{\epsilon} + \frac{\lambda(E_0) \lambda(\epsilon)}{\sqrt{\epsilon E_0}} \right] d\epsilon + \int_0^{E_0} \lambda(\epsilon) \frac{d\epsilon}{\epsilon^{3/2}} \int_0^\epsilon \lambda(\epsilon') \frac{d\epsilon'}{\epsilon'^{1/2}}, \quad (4)$$

$$\overline{y^2} = \overline{z^2} = \frac{\overline{r^2}}{3} - \frac{2\gamma}{3} \quad \text{and} \quad \overline{x^2} = \frac{\overline{r^2}}{3} + \frac{4\gamma}{3}, \quad (5)$$

with

$$\gamma = \lambda^2(E_0) + \int_0^{E_0} \left[\frac{\lambda^2(\epsilon)}{4E_0^{3/4} \epsilon^{1/4}} + \frac{\lambda(E_0) \lambda(\epsilon)}{E_0^{1/2} \epsilon^{1/2}} \right] d\epsilon + \frac{1}{4E_0^{3/4}} \int_0^{E_0} \lambda(\epsilon) \frac{d\epsilon}{\epsilon^{3/4}} \int_0^\epsilon \lambda(\epsilon') \frac{d\epsilon'}{\epsilon'^{1/2}}. \quad (5a)$$

The only quantity which has to be known to evaluate the averages is the mean free path λ , given by

$$\lambda(E) = \frac{1}{n\pi R^2(E)}, \quad (6)$$

where R is the hard-core radius defined by (2) and n is the number of atoms per unit volume. These formulas refer to a primary starting with energy E_0 in x direction at the origin of a rectangular x, y, z coordinate system. Since $\bar{y} = \bar{z} = 0$, the approximate width of the distribution perpendicular to the

x axis is $\sqrt{z^2}$ and the corresponding width in x direction is the square root of the variance, $\sqrt{x^2 - \bar{x}^2}$. To get an idea of the meaning of these quantities, let us assume that the distribution is Gaussian, which for a large number of hits is presumably quite a good approximation. Then the widths defined above are approximately the half-widths of this distribution, and the probability of finding an interstitial near the center is about twice that for finding it in the vicinity of the surrounding ellipsoid in Fig. 10. The probability for finding an interstitial inside the ellipsoid would be about 0.2. Thus the average density ρ near the center of the cascade should be the ratio of the number $\nu/5$ contained in the ellipsoid and the volume $4\pi z^2 \sqrt{x^2 - \bar{x}^2}/3$:

$$\rho(E_0) \cong \frac{0.05 \times \nu(E_0)}{z^2(E_0) [\bar{x}^2(E_0) - \bar{x}^2(E_0)]^{1/2}} \quad (7)$$

This value⁴⁴ may be somewhat misleading because the interstitial distribution is more concentrated than (7) shows. All the interstitials originate from the collision point (1) in Fig. 9. The distance of this point to the origin is on the average $\lambda(E_0)$ and the variance is $\lambda^2(E_0)$ according to the usual mean free path distribution. Thus a more reliable extension of the interstitial cascade can be calculated by disregarding the first path. The extensions in y and z directions and, of course, the center stay unchanged, whereas the variance in x direction decreases by $\lambda^2(E_0)$. Consequently,

$$\rho \cong \frac{0.05 \times \nu}{z^2 (\bar{x}^2 - \bar{x}^2 - \lambda^2)^{1/2}} \quad (7a)$$

The extension in x direction becomes smaller compared with that in Fig. 10. As a matter of fact, the

⁴⁴The maximum density for a Gaussian distribution is right in the center. Here the value 0.05 has to be replaced by $1/(2\pi)^{3/2} = 0.065$. The factor would be about 0.045 for an ellipsoid with axes of $\sqrt{2z^2}$, etc., which contains nearly 50% of the interstitials.

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Fig. 10. Distribution of Interstitials in a Cascade. The center $\bar{x}$ and the half-widths are shown in the figure.

shape of this distribution for large ν becomes rather spherical than ellipsoidal. The distributed $w(\vec{r})$ is a superposition of such spherical structures denoted by the broken circle in Fig. 10 distributed along the x axis according to the distribution of the first collision point, which obviously must give an ellipsoidal shape. Of course these considerations are only true for the structure of the interstitial cloud, but for large ν the first two vacancies may be disregarded.

Again the densities according to (7a) may be too small if there are internal correlations in the cascade. The two cascade branches originating in the first collision point contain on the average just $\nu/2$ interstitials. If now in every branch the interstitials are relatively close to each other, then the cascade contains two structures of relatively large density, the superposition of which gives the impression of a less densely packed spherical region. This behavior can be discussed when the energy dependence of the structural data is known in more detail. This point will be discussed later.

Evaluation of the Averages

For a given potential the mean free path can be obtained by Eqs. (2) and (6). Even for simple potentials such as a Bohr potential and a Born-Mayer potential the integrals for the averages are in general not elementary and would require numerical work. We will therefore use an approximation leading to simple analytical expressions which can easily be discussed. For the above mentioned potentials it will be shown that the deviations are of the order of 10%.

If the potential were a simple power potential,

$$\phi(r) = \frac{A}{r^\mu}, \quad (8)$$

all the integrals could easily be worked out, because according to (2)

$$R(E) = \left(\frac{2A}{E} \right)^{1/\mu} \quad (8a)$$

and

$$\lambda(E) = \frac{1}{n\pi R^2} = \frac{1}{n\pi} \left(\frac{E}{2A} \right)^{2/\mu}. \quad (8b)$$

If μ is larger than zero, all the integrals in (3-5) converge and are elementary.

The method will be illustrated for a potential of Bohr type,

$$\phi(r) = \frac{E_B}{2} \frac{a}{r} e^{-r/a}, \quad (9)$$

where E_B is a characteristic energy and a is the screening radius. The hard-core radius is defined by

$$\frac{E}{E_B} = \frac{a}{R} e^{-R/a}. \quad (9a)$$

The approximation will be made in the following way. If we calculate the averages for a given energy

$E = E_0$ we use an approximate power potential which has the same value and the same slope at $r = R(E)$. Thus a different potential is used for every initial energy E . Figure 11 shows some of these approximate potentials. Thus every calculation starts with the exact mean free path for the initial energy and the mean free paths for the subsequent collisions are determined by the approximate potential curve.⁴⁵ The approximate power potential is always larger than the exact value. Consequently, for given E the approximate hard-core radius is larger than the exact value and the approximate mean free path is underestimated. Thus the approximate averages are underestimated, too, because the effect of higher order collisions is suppressed somewhat. But since the mean free path decreases with energy, the influence of the higher order collisions is not very important.

Thus we use an approximate potential

$$\phi_a(r) = \phi(R) \left(\frac{R}{r} \right)^\mu \quad (10)$$

with

$$\phi'(R) = \phi'_a(R) = - \frac{\mu \phi(R)}{R}$$

⁴⁵ An approximation based on the use of a single approximation curve, for instance that fitted to $R/a = 1$, would give completely wrong results for other energies, because already the initial value of λ may be off by an order of magnitude. If $R(E)/a$ is about 3, Fig. 11 shows that the approximate R -value would be about $4.5 \times a$. Thus even the approximate λ value would be too small by a factor of 2. The deviations become worse for smaller energies.

Fig. 11. Bohr Potential (—) and Approximate Potentials Fitted to $R/a = 1$ (-----) and $R/a = 2$ (-.-.-).

or

$$\mu(R) = \mu(E) = - \left. \frac{d \ln \phi}{dr} \right|_{r=R} . \quad (10a)$$

The validity of the hard-core assumption is approximately given⁴⁰ by $\mu \gtrsim 2$. For the screened Coulomb potential (9), the result is

$$\mu = 1 + \frac{R}{a} . \quad (11)$$

Thus the hard-core law can be applied for $R/a \gtrsim 1$. For the energy dependence of the mean free path,

$$\lambda(\epsilon) = \lambda(E) \left(\frac{\epsilon}{E} \right)^{2/\mu} \quad (12)$$

is obtained and the averages are calculated to (Fig. 12)

$$\bar{x}(E) = \lambda(E) \frac{4 + 3\mu}{4 + \mu} , \quad (3'')$$

$$\overline{r^2}(E) = \lambda^2(E) \frac{4 + 3\mu}{2} , \quad (4')$$

$$\gamma(E) = \lambda^2(E) \frac{16(2 + \mu)^2}{(16 + 3\mu)(4 + \mu)} . \quad (5a')$$

An idea of the error introduced by the approximation is obtained by comparing these values with the exact results for the Bohr potential. As discussed in another paper,⁴⁰ the deviations should be most

Fig. 12a. The Dependence of the Averages on the Exponent μ of the Approximate Potential. Quadratic averages.

Fig. 12b. The Dependence of the Averages on the Exponent μ of the Approximate Potential. Half-widths and position of the cascade center.

serious for small energies ($R/a \gg 1$ or $\mu \gg 1$), because here the subsequent collisions play a more important role. In this case the following equations result for the Bohr potential:

$$\bar{x}(E) \approx \lambda(E) \cdot 2, \quad (3'')$$

$$\overline{r^2}(E) \approx \lambda^2(E) \left(\frac{7}{2} + \frac{2R}{a} \right) = \lambda^2(E) \frac{3 + 4\mu}{2}. \quad (4'')$$

The deviations for large μ are about 25% in $\overline{r^2}$ and 30% in $\bar{x}$. The error is much less for smaller μ , as is to be expected. For instance, the ratio of approximate to exact value for $\mu = 2$ is 0.96 for $\bar{x}$ and $\overline{r^2}$. Thus the deviations are only significant in the low-energy range ($\mu \gg 1$). Here the widths of the distribution are essentially determined by $\overline{r^2}$ alone (Fig. 12). Consequently, the widths are at most about 10% too small. For a pure exponential potential the approximation should be slightly better because this potential does not decrease as rapidly as the Bohr potential and the approximate potential gives a better fit. Altogether, we think that this approximation is good enough to give an idea of the cascade structure.

Of course, better approximations can be attempted by the following procedure. The above approximation can also be obtained by a power law for $\lambda(\epsilon)$ fitting $\lambda(E)$ and $\lambda'(E)$ at the initial energy. Now a better fit can be obtained by a superposition of two power laws taking into regard higher derivatives where still the required integrals can be easily evaluated. But on account of the uncertainty in the potential parameters the accuracy of the simple approximation is considered to be sufficient. It may be mentioned that this approximation is relatively bad for the average total traversed path $\bar{L}$, where L is the sum of all the distances $l_0 + l_1 + l_2 + \dots$ in Fig. 9. The exact value is given by

$$\bar{L} = \lambda \left(\frac{3}{2} + \frac{R}{a} \right) = \lambda \left(\frac{1}{2} + \mu \right),$$

whereas the approximate value is $\lambda(1 + \mu/2)$. This is due to the fact that in $\bar{L}$ the subsequent collisions are much more significant than in the widths.

The dependence of the interesting averages on the quantity μ has been plotted in Figs. 12a and 12b. For a Bohr potential μ is given by (11) as an implicit function of the initial energy. Since the formulae are more simply expressed by $R(E)$ than by E itself, everything will be discussed in terms of R , keeping in mind that for every potential decreasing with distance large R means low energy and vice versa. The relation between R and E depends on the assumed potential. The Bohr potential was only given as an illustrative example. The extension of the interstitial cascade is given in Fig. 13 for "high" energy

Fig. 13. Extension of the Interstitial Cascade (a) for $\mu = 2$, (b) for $\mu = 5$. The meaning of the contours is the same as in Fig. 10.

($\mu = 2$) and for "low" energy ($\mu = 5$). For low energies the effect of the first collision path is much more suppressed.

The validity⁴⁰ of the hard-core approximation can be expressed by the condition $\mu \gtrsim 2$. Consequently, all the discussions based on hard-core scattering are conclusive only below an energy limit given by this condition. For larger energies the collision process has to be investigated more closely. In the case of a screened Coulomb potential, there is for $R \ll a$ essentially Coulomb scattering where low energy losses during the collision are preferred and where the primary and the secondaries can well be discriminated.

Choice of a Potential for Copper

For "low" energies Huntington³⁶ has determined the parameters for a Born-Mayer potential in copper:

$$\phi_{BM}(r) = A e^{-r/a_{BM}} \quad (13)$$

with

$$A = 2.1 \times 10^4 \text{ ev} \quad \text{and} \quad a_{BM} = \frac{D}{13} \quad (13a)$$

Here D is the interatomic distance ($D = 2.56 \text{ \AA}$). This potential checks with the elastic data, which correspond to r values of about D . Further, it gives a displacement energy of the right order of magnitude corresponding³⁷ to values of r in the vicinity of $D/2$.

For "high" energies we will use a Bohr potential:

$$\phi_B(r) = \frac{E_B}{2} \frac{a_B}{r} e^{-r/a_B} \quad (14)$$

The range measurements in copper can be used^{39,40} for an approximate determination of the screening radius a_B . It turns out that a_B should be chosen slightly less than $D/10$. For the sake of simplicity we will take the same radius as that occurring in (13). Then the parameters in (14) have the values⁴⁰

$$a = a_B = a_{BM} = \frac{D}{13} = 0.197 \text{ \AA} \quad \text{and} \quad E_B = 12.8 \times 10^4 \text{ ev} \quad (14a)$$

This radius is about 1.6 times larger than the value originally suggested by Bohr. That about the same radii can be taken for both potentials is merely accidental and only applies for copper.

In the low-energy region ($D/2 \leq r \leq D$) the Bohr potential is about three times smaller than the Born-Mayer potential, and in the high-energy region ($r \approx a_B$) is about three times larger. Thus it does not seem unreasonable to use the sum of the two potentials (13) and (14) as a first approximation for the interaction potential which fits the experimental data for high and low energies. Therefore we use as interaction potential

$$\phi(r) = \left(A + \frac{E_B}{2} \frac{a}{r} \right) e^{-r/a} \quad (15)$$

and for a better fit at low energies require that

$$A^1 + \frac{E_B}{2} \frac{a}{D} = A \quad (15a)$$

Following (15a) the potential (15) has in the elastic region the same value as (13), and the deviations of the first and second derivatives which have to be used to calculate the elastic constants are off by about 5%. According to (15a),

$$A^1 \approx 1.6 \times 10^4 \text{ ev} \quad (15b)$$

For the following discussion the potential is written as

$$\phi(r) = \frac{E_B}{2} \left(\kappa + \frac{a}{r} \right) e^{-r/a} \quad (16)$$

with

$$E_B = 12.8 \times 10^4 \text{ ev} \quad , \quad a = \frac{D}{13} = 0.197 \text{ \AA} \quad , \quad \kappa = \frac{2A^1}{E_B} = 0.25 \quad (16a)$$

The relation for the hard-core radius $R(E)$ is then

$$\frac{E}{E_B} = \left(\kappa + \frac{a}{R} \right) e^{-R/a} \quad (17)$$

Equation (10) shows the power $\mu(E)$ of the approximate potential to be

$$\mu = \frac{1}{1 + \kappa \frac{R}{a}} + \frac{R}{a} \quad (18)$$

The potential (16) is essentially fitted to the elastic data. But it also applies well to intermediate and high energies. The displacement energy for this potential is about 27 ev. (The displacement energy can be evaluated by taking³⁷ $R \approx D/\sqrt{3}$.) The observed^{39,40} range in copper is 160 Å for an energy of 4.1×10^4 ev. The theoretical range⁴⁰ can be approximated by $\sqrt{r^2}$ and is calculated following (4') to 200 Å. Thus the agreement with experimental data for low and high energies is not too bad. Figure 14 shows a plot of R and μ vs energy.

Interstitial Densities

The interstitial density ρ now can be calculated as a function of initial energy E . By using (1) and (7a), one gets

$$\rho(E) = \frac{5 \cdot 10^{-2} E}{2 E_d \bar{x}^2 (E) (\bar{x}^2 - \bar{x}^2 - \lambda^2)^{1/2}}$$

Fig. 14. Hard-Core Radius $R(E)$ and the Power $\mu(E)$ of the Approximation Potential as Functions of Energy. The energy marks refer to the displacement energy (27 eV) and to the energy used in the range measurements (4.1×10^4 eV) for Cu.

Introducing (17) and (6) results in

$$\rho(E) = C \left(\frac{R}{a} \right)^6 \left(\kappa + \frac{a}{R} \right) e^{-R/a} \Gamma \quad (19)$$

Here the constant C is given by

$$C = \frac{5.10^{-2} E_B}{2 E_d \lambda_a^3} ,$$

where $\lambda_a = 1/\pi\pi a^2$ is the mean free path for $R = a$. For copper, $\lambda_a \approx 100 \text{ \AA}$ and the numerical value of C is

$$C = 1.18 \times 10^{20} \text{ cm}^{-3} . \quad (19a)$$

If it is desired to refer ρ to the atomic density, C has to be multiplied by the atomic volume $D^3/\sqrt{2}$:

$$CD^3/\sqrt{2} \approx 1.4 \times 10^{-3} . \quad (19b)$$

Further Γ is an abbreviation for

$$\Gamma = \frac{\lambda^3(E)}{z^2(E) (\bar{x}^2 - \bar{x}^2 - \lambda^2)^{1/2}} , \quad (19c)$$

which depends only on μ .

The result is plotted in Fig. 15. The interstitial density shows a maximum of about 5 at. % for energies near 1300 eV where $R \approx 4a$. Such a cascade would contain 24 interstitials and about the same

Fig. 15. Interstitial Density as a Function of Energy.

number of vacancies. This is a very high density from an atomistic point of view; it corresponds to an average distance between interstitials of about 2.5 interatomic distances. The linear dimensions of this cascade are 8 atomic distances and the affected volume with such a high density would contain about 100 atoms. The absolute extension of this cascade would be considerably larger. As an idea of the dimensions of the cascade, it may be assumed that the distribution is homogeneous within a rotation ellipsoid around the x axis centered at $\bar{x}$. Then the axes of the ellipsoid are given by $\sqrt{5(\bar{x}^2 - \bar{x}^2)}$ and $\sqrt{5z^2}$. This model would lead to a factor of 0.02 in Eq. (7) and roughly decrease the densities by a factor of 2. But this assumption presumably leads to an underestimate of the maximum densities occurring in a cascade. The affected volume in this model would be about 10^3 atomic volumes for the energy in question.

At first it seems surprising that the density shows a maximum. For an initial energy above the maximum, it is known that the cascade can be resolved into a superposition of smaller subcascades belonging to smaller energies. These subcascades have partly higher densities than those resulting for the total cascade. But the subcascades have a distribution which altogether gives an average density for the total cascade which is less than that for the subcascades themselves. (This behavior is quite analogous to the small average density of a gas consisting of drops with relatively high density.) If, on the other hand, the initial energy is at or below the maximum, the subcascades have smaller densities than that calculated for the total cascade. In this case there must be an essential overlap between the subcascades in order to increase the total density above the smaller densities of the subcascades. This behavior is sketched in Fig. 16 for various initial energies. Here it is assumed that the primary causes two subcascades, each possessing half the primary energy. The elliptical content of the subcascades has been taken using the homogeneous elliptical distribution. The numerical values have been chosen such that the volume of all ellipsoids is the same. It has to be imagined that this distribution rotates about the primary direction and that the origin of the production of the subcascades is distributed along the primary direction according to a mean free path law. This altogether would then give the corresponding elliptical distribution of the total cascade.

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Fig. 16. Overlap Between Subsequent Cascades.

According to Fig. 16 the overlap increases with decreasing energy. For the energy corresponding to the maximum in the density the overlap just begins to reach the central regions. But also for relatively high energies the overlap is not negligible. Altogether one gets the impression that the subcascades cannot be treated as more or less independent, that is, not overlapping, structures. It might be possible for higher energies where the central regions are not affected but would certainly be a bad approximation for energies less than 1300 ev.

It must be mentioned that the introduction of the Born-Mayer potential is rather essential with regard to the numerical values. The Bohr potential alone would qualitatively show the same behavior of density with energy, but the maximum density would be smaller by a factor of about 5 and the corresponding energy would be lower by a factor of about 2. The introduction of the additive Born-Mayer potential makes the mean free path smaller than that of the Bohr potential itself, and this effect is more pronounced at lower energies, giving a mean free path on the order of the atomic spacing for energies near E_d . Of course the calculations do not apply for energies below some hundred ev for two reasons: first, the equations would have to be replaced by a more refined theory including energy-dependent displacement probabilities; second, the mean free path assumption breaks down because of the influence of lattice structure.

Correlation in the Cascade

It is easy to calculate another average which elucidates the correlation between the interstitials, namely, for $\vec{\Delta} = \vec{r} - \vec{r}'$, where $\vec{r}$ and $\vec{r}'$ refer to any two particles in the cascade. The average value of $\vec{\Delta}$

is evidently zero. The quadratic average gives an idea about the average distances between interstitials in the cascade. If the particles were distributed independently, then

$$\overline{\Delta_{\text{ind}}^2} = \overline{r^2} - \overline{r'^2} - 2\overline{r \cdot r'} = 2(\overline{r^2} - \overline{x^2}) , \quad (20)$$

where it is assumed that the initial direction is parallel to the x axis. If $\overline{\Delta^2}$ is smaller than the value given by (20), then the particles have a tendency to be nearer to each other than would correspond to the average density, as in a gas consisting of drops or in a gas with attractive forces. If $\overline{\Delta^2}$ is larger, then the particles tend to avoid each other as the electrons in metals or the particles of a gas with repulsive forces.

We have seen already by subtracting the first collision path that $\overline{\Delta^2}$ should be smaller than $\overline{\Delta_{\text{ind}}^2}$. Now we shall make this argument quantitative. The value of $\overline{\Delta^2}(E)$ is defined by

$$\overline{\Delta^2}(E) = \frac{2}{\nu(\nu-1)} \sum_{i \neq k=1}^{\nu} \overline{(\vec{r}^i - \vec{r}^k)^2} . \quad (21)$$

Here $\vec{r}^i$ and $\vec{r}^k$ are the final positions of the $\nu(E)$ interstitials, the sum extends over all different pairs of interstitials, and the factor $\nu(\nu-1)/2$ gives the proper normalization. For the sake of simplicity we neglect unity in comparison with ν so that the treatment is only correct for large ν . The contribution in the sum (21) can be split up following the cascade process after the first collision. The interstitials belong either to the subcascade due to the scattered primary with energy E_1 or to the knocked-on secondary with energy E_1' (Fig. 9). The numbers contained in the subcascades are $\nu(E_1)$ and $\nu(E_1')$. The distribution of the energies is

$$\delta(E_1 + E_1' - E) \frac{dE_1 dE_1'}{E}$$

according to the second section of this paper. The contribution to (21) by one pair not belonging to the same subcascade is for given energies just $\overline{r^2}(E_1) + \overline{r^2}(E_1')$ because the average vectors are perpendicular to each other. This has to be multiplied by $\nu(E_1)\nu(E_1')$ to get the contribution of all pairs. The contributions of pairs belonging to the same subcascade are then $\nu^2(E_1)\overline{\Delta^2}(E_1)/2$ and $\nu^2(E_1')\overline{\Delta^2}(E_1')/2$. Consequently, summing the various contributions and integrating over the energy distribution results in an integral equation for $\overline{\Delta^2}(E)$ which can be simplified due to the symmetry of the energy distribution

$$\overline{\Delta^2}(E) = \int_0^E \left[4\nu(E_1) \nu(E-E_1) \overline{r^2}(E_1) + 2\nu^2(E_1) \overline{\Delta^2}(E_1) \right] \frac{dE_1}{E\nu^2(E)} , \quad (22)$$

or introducing (1)

$$\overline{\Delta^2}(E) = \int_0^E \left[4E_1(E-E_1) \overline{r^2}(E_1) + 2E_1^2 \overline{\Delta^2}(E_1) \right] \frac{dE_1}{E^3} . \quad (22a)$$

The inhomogeneity can be calculated by the approximation of the third section of this paper, fitting the power μ to the initial energy

$$\int_0^E 4E_1 (E - E_1) \overline{r^2}(E_1) dE_1 = \overline{r^2}(E) \frac{2\mu^2}{(2 + \mu)(4 + 3\mu)}. \quad (23)$$

The solution of the integral equation is relatively simple, and the following is obtained:

$$\overline{\Delta^2}(E) = \overline{r^2}(E) \frac{2\mu^2}{(2 + \mu)(4 + \mu)}. \quad (24)$$

It is easily seen that (24) solves the integral equation (μ depends only on initial energy E). The solution of the homogeneous equation would be proportional to $1/E$ and must be excluded on physical grounds.⁴⁶ This value has to be compared with $\overline{\Delta_{ind}^2}(E)$ according to (20), which is calculated by the same approximation. Typical values are listed below; they show that for large energies there is some tendency for cluster formation, whereas for somewhat lower energies the distribution is not far from being independent:

μ	$\overline{\Delta^2}/\overline{\Delta_{ind}^2}$
2	0.37
3	0.55
4	0.67
5	0.75
6	0.8
7	0.85

The first summand in (22a), abbreviated by δ^2 , is the contribution to $\overline{\Delta^2}$ from the particles belonging to different branches after the first collision; the second term, $2\delta'^2$, is twice the contribution from any one of the branches. The ratio δ^2/δ'^2 also gives an idea of the overlap between the subcascades. Using (23) and (24), one gets $\delta^2/\delta'^2 = 1 + 4/\mu$. For small μ ($\mu \gtrsim 2$) the average distances between the subcascades are somewhat larger than the corresponding distances in the cascades; for larger values of μ they are almost equal. This also shows the increase of overlap with decreasing initial energy. But since the ratio δ^2/δ'^2 is always of order of magnitude 1 for the energy range of interest, the overlap is always appreciable.⁴⁷

⁴⁶For large μ values, $\overline{\Delta^2} \approx 2\overline{r^2}$ and also $\overline{\Delta_{ind}^2} = 2\overline{r^2}$ because $\bar{x}$ can be neglected. This is a case where λ is nearly constant and a large number of collisions are involved; then one knows that the distributions are almost independent and Gaussian.

⁴⁷For very high energies $R < a$ the situation would change. Here Coulomb scattering with preferred low energy transfer would be prevalent. Consequently, the subcascades are relatively small and presumably separated enough for them to be treated as independent. The hard-core approximation would not apply. Further, ionization effects must be taken into consideration.

Conclusions

According to the foregoing the overlap does not seem to be neglectable. Consequently, an attempt to treat a single primary event as a cascade consisting of subcascades does not seem promising. A better theoretical treatment would have to regard the event as a whole, for instance assuming a homogeneous elliptical distribution. For every primary event of energy E there are a certain number ν of interstitials and vacancies and a cascade volume V_c . Figure 17 shows a plot of V_c (in atomic volumes) vs. energy. The use of the approximation underestimates the volume, especially for low energies. In the very low energy region the values would not be very dependable because the lattice structure has an essential influence there.

So far the vacancies have not been discussed, and only the interstitial distribution has been treated. But for cascades with large ν the vacancy distribution should be similar to that of the interstitials, and the error when assuming the same distribution should not be great.

The high defect densities, especially for intermediate energies, should result in an interaction between those defects produced by one primary. It is possible that the structure can be changed by low-energy effects, such as crowdion motions^{37,48} which tend to shoot out interstitials over distances larger than the dimensions of the cascade. This would show up especially for intermediate primary energies for which the linear dimensions of the cascade are on the order of 10 atomic distances. This could lead to cascades with an excess of vacancies, and would essentially lead to Brinkman's description of a cascade.⁴⁹

It is by no means clear that the cascade structure discussed above is a stable structure for intermediate and high energies. The primary energy which is set free in the cascade volume and the close distance between defects may well lead to an appreciable self-annealing, drastically reducing the damage

⁴⁸A. Seeger, *Second United Nations International Conference on the Peaceful Uses of Atomic Energy* (Geneva, 1958), paper No. 998.

⁴⁹J. A. Brinkman, *Am. J. Phys.* **24**, 246 (1956).

Fig. 17. Volume of the Cascade V_c (in Atomic Volumes) and Number of Pairs $\nu(E)$ vs Energy.

expected on account of the simple theory. But it should be remembered that the time for the development of the cascade is very short. This means that the cascade as pictured here can be taken as a first step, whereas annealing effects require much longer times and can be treated separately, with the picture developed here taken as initial configuration.

The foregoing calculations were based on the approximation of the scattering process by hard-core scattering. The deviations introduced by this approximation are difficult to treat.⁵⁰ The general trend is the following. The differential cross section for energy transfer is smaller than the corresponding hard-core cross section for large energy transfers and is larger for low energy transfers. As an example, for a Bohr potential and $R/a = 1$ (or $\mu = 2$) the high energy limit is about 50% smaller. This deviation becomes smaller with decreasing energy, being still of the order of 20% for $\mu \approx 10$. In the classical scattering theory the cross section diverges for small energy transfers whenever the potential extends to infinity. Physically this divergence does not cause trouble because there are several reasons for a natural cutoff at low energies as determined by either a maximum impact parameter of about half the atomic distance or by taking into regard quantum mechanical corrections. Generally the stopping power or the energy loss per unit length is larger for the real potential than for the corresponding hard-core law. But even for $\mu \approx 2$ the deviation is only 50% and this deviation decreases with decreasing energy. Altogether the deviations from the assumed hard-core law are not considered to be serious for $\mu \gtrsim 4$, so that the foregoing results should be qualitatively correct. For larger energies ($\mu \gtrsim 2$) the results should still be qualitatively correct, but here one should account for the fact that a fraction of the interstitials produced are formed as small clusters of vacancy-interstitial pairs, especially along the first part of the collision history of the primary until it undergoes a collision with large angle deflection.

The high densities obtained for copper are to a large extent due to the influence of the Born-Mayer potential which describes the closed-shell repulsion. This implies that for a material such as germanium, where the closed-shell repulsion is not important and where the Bohr potential is approximately the same, the densities are substantially less (by about a factor of 5, as mentioned earlier).

APPROXIMATE TREATMENT OF ANNEALING WITH A SPECTRUM OF ACTIVATION ENERGIES AND FIRST-ORDER KINETICS

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Some recent experimental work in the annealing of radiation damage^{51,52} has indicated that the annealing process is not simply activated. The purpose of this paper is to present in a convenient form a simple approximation to the problem of the annealing of defects having a spectrum of activation energies.

⁵⁰For a detailed discussion, see "Classical Scattering Theory for Interatomic Collisions," this report.

⁵¹T. H. Blewitt *et al.*, p 603, in *Dislocations and Mechanical Properties of Crystals*, Wiley, New York, 1957.

⁵²G. D. Magnuson, W. Palmer, and J. S. Koehler, *Phys. Rev.* 109, 1990 (1958).

While the work presented here was independently performed by the authors, several other similar treatments have been published.⁵²⁻⁵⁴

The physical model to be considered is that of a number of defects which are introduced in some way into a solid and which are found to anneal out in some elevated temperature range. The defects are assumed to be independent and to display a range of apparent activation energies for annealing. (The energy may be a trapping energy or an energy of motion.) Specifically, let

$$n(E, t) dE \quad (1)$$

be the total number of defects at time, t , whose apparent activation energies lie in the energy range E to $E + dE$ and assume the following rate equation to hold:

$$-\frac{\partial n(E, t)}{\partial t} = \kappa(E, T) n(E, t) \quad (2)$$

For convenience the spectrum of (1) is normalized to unity at time $t = 0$; then

$$\int_0^\infty n(E, 0) dE = 1 \quad (3)$$

The experimentally important quantity is usually the fraction of the defects remaining at any time t , given by

$$f(t) = \int_0^\infty n(E, t) dE \quad (4)$$

This general model can be applied to the specific case, usually of greatest interest, for which the temperature is taken to be independent of the time, that is, isothermal annealing. Then

$$f(t) = \int_0^\infty n(E, 0) e^{-\kappa(E, T)t} dE \quad (5)$$

This form is also applicable to pulse-annealing experiments, with the zero of time then referring to the beginning of a given pulse. Further, for the present discussion, which is supposed to be applicable to atomistic processes, we take the rate constant to be of the form

$$\kappa(E, T) = \nu e^{-E/kT} \quad (6)$$

In Eq. (6) ν is a frequency factor and k is the Boltzmann constant.

If the original distribution $n(E, 0)$ is strongly peaked, Eq. (5) gives the usual first-order, singly activated exponential behavior in time. Thus, for

$$n(E, 0) = \delta(E - E_1) \quad (7)$$

$$f(t) = e^{-\nu t e^{-E_1/kT}} \quad (8)$$

⁵³W. Primak, *Phys. Rev.* 100, 1677 (1955).

⁵⁴A. M. Freudenthal and H. Geiringer, p 228, esp p 276, in *Handbuch der Physik*, vol VI (S. Flügge, ed.), Springer-Verlag, 1958.

However, the cases of greatest interest here are those for which $n(E,0)$ is "spread out" over an energy range much larger than kT . There is then the difficult problem of extracting some information about $n(E,0)$ from a knowledge of the behavior of $f(t)$, that is, an integral over $n(E,0)$ with a time-dependent kernel, $e^{-\kappa t}$. Essentially the same problem has been met in the classical treatment of relaxation spectra,⁵⁴ and approximate methods have been devised for obtaining the spectrum based on the use of derivatives of the experimental data for $f(t)$. In the present case it is not felt that consideration of higher derivatives than the first would be justified, in view of normal experimental errors. However, it is necessary to go to at least the first derivative since the kernel in Eq. (5), that is, $e^{-\kappa(E,T)t}$, regarded as a function of E , is not peaked, while the kernel in the integrand of the derivative with respect to the logarithm of the time is peaked. Thus,

$$-\frac{df(t)}{d \ln t} = \nu t \int_0^\infty n(E,0) \left[e^{-\nu t e^{-E/kT}} e^{-E/kT} \right] dE, \quad (9)$$

the bracketed expression has a maximum in energy at an energy E_0 , given by

$$E_0 = kT \ln \nu t, \quad (10)$$

and it might be guessed that a first estimate for the value of the integral would involve some factors multiplying $n(E_0,0)$.

Proceeding more carefully, Eq. (9) may be written

$$-\frac{df}{d \ln t} = \nu t \int_0^\infty e^{-F(E)} dE, \quad (11)$$

where

$$F(E) \equiv \frac{E}{kT} + \nu t e^{-E/kT} - \ln n(E,0). \quad (12)$$

Expanding $F(E)$ in a Taylor series about E_0 ,

$$F(E) = F(E_0) + (E - E_0) F'(E_0) + \frac{(E - E_0)^2}{2} F''(E_0) + \dots, \quad (13)$$

and defining E_0 by the requirement

$$F'(E_0) = 0, \quad (14)$$

it may be shown that

$$-\frac{df}{d \ln t} \approx \nu t e^{-E_0/kT} e^{-\nu t e^{-E_0/kT}} \frac{n(E_0,0) \sqrt{2\pi}}{\sqrt{\frac{\nu t}{(kT)^2} e^{-E_0/kT} + \frac{(1 - \nu t e^{-E_0/kT})^2}{(kT)^2} - \frac{n''(E_0,0)}{n(E_0,0)}}} \quad (15)$$

with

$$1 - \nu t e^{-E_0/kT} = kT \frac{n'(E_0, 0)}{n(E_0, 0)} \quad (16)$$

The approximation of Eqs. (15) and (16) is obtained by using only the terms shown explicitly in Eq. (13) in the expansion of $F(E)$. In Eqs. (15) and (16)

$$n'(E_0, 0) \equiv \left[\frac{dn(E, 0)}{dE} \right]_{E=E_0}, \quad n''(E_0, 0) \equiv \left[\frac{d^2 n(E, 0)}{dE^2} \right]_{E=E_0} \quad (17)$$

If the spectrum $n(E, 0)$ is flat in the region of E_0 , it may be acceptable to introduce the approximations

$$kT \frac{n'(E_0, 0)}{n(E_0, 0)} \ll 1, \quad (kT)^2 \frac{n''(E_0, 0)}{n(E_0, 0)} \ll 1, \quad (18)$$

which lead to a first-order approximation to Eqs. (15) and (16),

$$-\frac{df}{d \ln t} \simeq kT n(E_0, 0), \quad (19)$$

$$E_0 \simeq kT \ln \nu t, \quad (20)$$

corresponding to the guess made in Eq. (10).⁵⁵ In the following, consideration will be given to some of the features of the approximation (19) and (20) but not to the possibilities of a better treatment through Eqs. (15) and (16).

Equations (19) and (20) provide a method for obtaining an approximate spectrum over a certain energy range [as determined from the range of experimental times through Eq. (20)] by taking the derivative of the experimental data with respect to the logarithm of the time. This also suggests that the experimental results be plotted as a function of the logarithm of time, since linear behavior on such a plot indicates a flat region of the spectrum. Two simple tests of this approximation are illustrated in Figs. 18 and 19. In Fig. 18 the true annealing is assumed to be uniquely activated, that is, the true $n(E_0, 0)$ is a delta function, in this case assumed to be centered at $E_1/kT = 30$. Thus, the true annealing follows the form of Eq. (8), and $-df/d \ln t$ can be accurately obtained. From Eqs. (19) and (20) an approximate form for $n(E_0, 0)$ can be obtained; this is shown in Fig. 18. It may be seen that the approximate spectrum is spread out by something like $2kT$ in energy. This is further illustrated by a second example. Assuming

⁵⁵ Actually, the treatment outlined gives a factor of $\sqrt{2\pi}/e$, where $e = 2.7183$, on the right-hand side of Eq. (19); but this has been dropped since the spectrum would not be properly normalized if this factor is included. Even so, the distribution $n(E_0, 0)$ of Eq. (19) is not quite properly normalized. Direct integration shows that a normalizing factor of $f(1/\nu)$ is needed on the right-hand side of Eq. (19). However, this must be very near unity for all cases of interest.

Fig. 18. Comparison of the Approximate Spectrum with the True Spectrum, a Delta Function.

Fig. 19. Comparison of the Approximate Spectrum with the True Spectrum, a Double-Block Function.

a double-block spectrum of the form

$$n(E,0) = \begin{cases} 0, & E < E_1, \\ c, & E_1 \leq E \leq E_2, \\ 0, & E_2 < E < E_3, \\ c, & E_3 \leq E \leq E_4, \\ 0, & E_4 < E, \end{cases} \quad (21)$$

where

$$c \equiv \frac{1}{E_4 - E_3 + E_2 - E_1},$$

the function $-df(t)/d \ln t$ may be calculated directly from Eq. (9):

$$-\frac{df}{d \ln t} = ckT \left(e^{-\nu t} e^{-E_2/kT} - e^{-\nu t} e^{-E_1/kT} + e^{-\nu t} e^{-E_4/kT} - e^{-\nu t} e^{-E_3/kT} \right). \quad (22)$$

From Eq. (22), $-df/d \ln t$ may be calculated for all times (given a choice for ν and for kT); then, from Eq. (19) an approximate spectrum may be computed at all energies, as obtained from the times through Eq. (20). The agreement between exact and calculated spectra, as shown in Fig. 18, seems quite good for such a crude approximation, especially when it is remembered that [from Eq. (18)] the approximate form is expected to be "fuzzed out" over a range of one to two kT , which, for the case of Fig. 19, is 0.03 to 0.06 ev.

Figure 20 shows a direct application of this approximation to experimental data. Three isothermal annealing curves for resistivity quenched into copper-aluminum alloy taken by Wechsler and Kernohan⁵⁶ have been treated by this method, with approximate resulting spectra shown in Fig. 20. This is only presented here to illustrate how the present method may be used. Note that for the system investigated by Wechsler and Kernohan the temperatures listed in Fig. 20 correspond to greatly different annealing rates; for example, at 45.1°C the system requires 10,000 min to reach a stage achieved at 90.0°C in about 500 min. The point to be made here is that from this type of analysis a clue to the underlying physical process may be obtained. If the approximate spectra of Fig. 20, for example, are regarded as sufficiently similar, it may be argued that the assumptions of the present model are met in this system, that is, independent defects annealing in first order. In this particular case it would seem that perhaps there are just two distinct species (taking into account the "fuzzing out" as illustrated in Fig. 18), the one of apparent activation energy around 1.1 ev occurring in somewhat greater numbers than the one of apparent activation energy around 1.2 ev. Of course, this is only a preliminary suggestion, and further data may reveal that the similarity of the spectra of Fig. 20 is accidental or may be explained in some other manner.

As a last point it should be mentioned that, if a physical process exists corresponding to this model in which the true spectrum is actually slowly varying over a significant energy range, during the annealing process the apparent activation energy will rise with time. For example, in an isothermal anneal of a

⁵⁶M. S. Wechsler and R. H. Kernohan, "Lattice Defects in a Copper-Aluminum Alloy," to be published in *Acta Met.*

Fig. 20. Approximate Spectra from Annealing Data on a Quenched Copper-Aluminum Alloy (Wechsler and Kernohan, ref 56).

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flat spectrum, the apparent activation energy will (over the time range corresponding to the flat region of the spectrum) just increase logarithmically in time, as shown by Eq. (20). Although the analysis of other annealing methods, and particularly of the "slope method,"⁵² on the basis of this model is too complicated to present here, it is true that the model predicts that any method of determining the activation energy at any stage of the annealing will tend to show a progression of energies following a law representing a generalization of Eq. (20).

DISLOCATION INTERACTIONS

EFFECT OF FAST NEUTRON BOMBARDMENT
AT VARIOUS TEMPERATURES UPON THE
YOUNG'S MODULUS AND INTERNAL
FRICTION OF COPPER

D. O. Thompson

V. K. Paré

It has been shown in previous work^{1,2} that the dislocation contribution to the elastic modulus and internal friction of copper crystals is extremely sensitive to radiation-produced defects, and that the variation of these quantities during irradiation at room temperature is well described by a simple theory of pinning. Since measurements are made on samples having relatively low dislocation densities ($\sim 10^7$ per cm^2), the defects must migrate an appreciable distance to reach the dislocations. Furthermore, the amplitude of sample vibration is kept very small, so that motion of the dislocations during the measurement is completely negligible. Consequently, it was felt that the dislocations would act as a stationary, highly sensitive detecting network for defects which migrate by diffusion or other processes. Therefore, a series of bombardments at various temperatures was begun during the past year with the hope that the damage rates measured at the various temperatures would provide information concerning the spectrum of defects and their activation energies for mobility. Even though the experiments have not been completed, several interesting results have been discovered and will be discussed briefly. A more complete description of these experiments will appear shortly in the open literature.³

In Fig. 21 are shown the results of different constant-temperature neutron bombardments upon the Young's modulus. The bombardment temperatures are noted in the figure. The symbol E in the ordinate is the measured modulus at time t , E_0 is the measured modulus at zero time, and E_e is the elastic or "saturated" modulus (with the dislocations completely pinned by defects).

These are all measured at the bombardment temperature. Since it has been established that the dislocation contribution to the measured modulus is a function of temperature, at least at this measurement frequency, the ordinate in this figure has been chosen to represent a normalized fractional completion of the modulus change as a function of time (or integrated neutron flux) at several different temperatures. Consequently, each of the curves in the figure would approach unity if the bombardments at the various temperatures had been extended sufficiently long. Conversely, for a given bombardment time, the fractional completion value gives a relative measure of the governing defect rate constant as a function of temperature. It should be noted that the internal friction data obtained in these runs are entirely consistent with the observed modulus results.

It has been shown previously¹ that radiation-induced changes in the modulus and decrement can be described quite well by the equations

$$\frac{1}{E(t)} = \frac{1}{E_e} + \left(\frac{1}{E_0} - \frac{1}{E_e} \right) \cdot \frac{1}{(1 + \gamma t)^2} \quad (1)$$

Fig. 21. Fractional Completion of Modulus Change as a Function of Bombardment Time. E is Young's modulus; E_0 is its initial value, and E_e is the final value, after the irradiation effect is fully saturated.

¹D. O. Thompson and D. K. Holmes, *J. Appl. Phys.* 27, 713 (1956).

²H. Dieckamp and A. Sosin, *J. Appl. Phys.* 27, 1416 (1956).

³D. O. Thompson and V. K. Paré, to be published.

and

$$\delta(t) = \delta_e + \frac{\delta_0 - \delta_e}{(1 + \gamma t)^2}, \quad (2)$$

in which $E(t)$ and $\delta(t)$ are the measured modulus and decrement values at time t , E_e and δ_e are the final, or "saturated," values of the same quantities, and E_0 and δ_0 are the values at zero time. The quantity γ is the "rate constant" of immediate interest, for it is proportional to the number of defects which migrate to the dislocations at the bombardment temperature. Hence a plot of γ vs temperature is essentially a plot of the integral of the defect spectrum from $T = 0$ to the neighborhood of the bombardment temperature.

In order to obtain γ as a function of temperature, the data of Fig. 21 have been plotted according to Eq. (1) in Fig. 22. It is assumed, of course, that Eq. (1) is valid over the whole temperature range covered, as well as at room temperature. The symbols used in this plot have the same meanings as those used previously. If Eq. (1) were obeyed exactly, the lines in Fig. 22 would be straight with slope γ . As can be seen from the plot, the lines actually show appreciable curvature in the early part of the bombardment and later become straight. It can be shown³ that the curvature can be accounted for very reasonably by assuming that

Fig. 22. $\{[(E_e - E)/E] / [(E_e - E_0)/E_0]\}^{-1/2} \equiv \gamma^{-1/2}$ as a function of bombardment time at various temperatures. The symbols have the same meanings as in Fig. 21.

two or more different types of dislocations are being pinned, and further, that the initial slope is the average of the values of γ for the different types of dislocations weighted according to their contributions to the modulus change. This weighted value of γ was felt to be the most suitable one for representing the temperature dependence of γ .

The averaged values of γ are plotted as a function of bombardment temperature in Fig. 23. There is included a point previously obtained⁴ in the Hole 12 cryostat at 20°K. A logarithmic scale has been chosen so as to display the most significant feature of the plot — the extremely large variation of γ over the temperature range

⁴D. O. Thompson, T. H. Blewitt, and D. K. Holmes, *J. Appl. Phys.* 28, 742 (1957).

Fig. 23. Pinning Rate Constant γ as a function of Temperature.

covered. This variation is by a factor of about 40,000 between bombardments at 20 and 308°K. Even at 100°K the number of pinning defects is lower by a factor of about 40 than at 308°K.

Presumably, the most important factors determining the pinning rate constant displayed in Fig. 23 are the values of activation energy required for migration of the defects to the dislocations and the relative number of each kind produced in the bombardment. As will be discussed more fully elsewhere,³ it is possible to conclude from the present data that a continuous activation energy distribution is consistent with the data within the temperature interval covered by these experiments. It is also possible to conclude that, in terms of the number of defects which migrate at room temperature, only 2 to 3% of the defects are thermally mobile at 100°K. No evidence for a unique activation energy has been uncovered in the temperature intervals measured to date.

It is proposed that during the next year constant-temperature bombardments will be made in two very important temperature intervals. The first is from 20 to about 78°K, and the second is from about 250 to 320°K. Significant "annealing" stages have been observed in the modulus in these ranges^{3,4,5} as well as in resistivity measurements. It is felt that if unique activation energies are to be observed, it will be in these temperature regions.

Another series of measurements has been begun recently which appears quite interesting. Hasiguti⁶ has found two internal friction peaks in deformed copper which are claimed to be due to trivacancies and divacancies produced by the deformation, and which anneal out readily at room temperature. Techniques have recently been developed at ORNL so that the sample is deformed in torsion at liquid nitrogen temperature in the internal friction apparatus and never allowed to warm to room temperature. Only preliminary measurements have been made using this scheme, but it appears, at least qualitatively, that the results do not

agree entirely with Hasiguti's. It is hoped, of course, that experiments of this kind might provide a link with radiation damage studies, and they will therefore be continued during the coming year.

DISLOCATION CONTRIBUTION TO THE TEMPERATURE DEPENDENCE OF THE INTERNAL FRICTION AND YOUNG'S MODULUS OF COPPER

D. O. Thompson

D. K. Holmes

Studies of the Bordoni internal friction peaks and the associated internal friction background in copper due to dislocations have been completed. These studies have proved of value in subsequent measurements of neutron damage rates at various low temperatures. An abstract of the published paper follows:

Dislocation Contribution to the Temperature Dependence of the Internal Friction and Young's Modulus of Copper.⁷ D. O. Thompson and D. K. Holmes. — A study of the amplitude-independent internal friction and Young's modulus in copper from 14°K to room temperature, both before and after neutron irradiation, indicates that there are two dislocation components in these quantities. These have been tentatively identified as a relaxation component, studied in detail theoretically by Seeger, and a background component which appears to be characteristic of Koehler's bowing mechanism. It is felt that these two components are probably quite intimately related, for the background internal friction rises at just slightly higher temperatures than the maximum of the individual relaxation processes, and the activation energy of the background process is about twice the kink energy obtained from Seeger's theory. Moreover, the Bordoni, or relaxation, spectrum is shown to be considerably more complex than has been previously indicated, in that there appear to be at least four principal relaxations. As a result of the analysis attempted in the present work, it appears that the more obvious difficulties of Seeger's theoretical treatment are alleviated.

⁵A. Sosin and L. L. Bienvenue, *Bull. Am. Phys. Soc.* [2]4, 169 (1959).

⁶R. R. Hasiguti, AEC Conference on Radiation Damage held at Atomics International, Canoga Park, Calif., Oct. 15 and 16, 1958.

⁷D. O. Thompson and D. K. Holmes, *J. Appl. Phys.* 30, 525-41 (1959).

ELASTIC CONSTANT-INTERNAL FRICTION
SPECTROMETER

D. O. Thompson

A spectrometer for the continuous measurement of the Young's modulus and internal friction of a metal sample has been developed. Details of the apparatus have been published, and an abstract follows:

⁸D. O. Thompson and F. M. Glass, *Rev. Sci. Instr.* 29, 1034-40 (1958).

Elastic Constant-Internal Friction Spectrometer.⁸

D. O. Thompson and F. M. Glass. — An elastic constant-internal friction spectrometer has been developed which has proved to be very useful in measurements which must last over extended periods of time as well as in measurements which require a high degree of resolution. The essential feature of the spectrometer is the fact that it holds the sample in oscillation at its resonance frequency at a preset strain amplitude and measures the internal friction of the sample through a measurement of the driving force necessary to maintain the preset amplitude.

LOW-TEMPERATURE IRRADIATION STUDIES

ANNEALING KINETICS OF NEUTRON-IRRADIATED ALUMINUM AND COPPER

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

Introduction

The earliest concepts of radiation damage in metals assumed that fast neutrons interacted with atoms in their equilibrium position, resulting in their displacement and the formation of vacant lattice sites and interstitial atoms. Since theoretical considerations indicated interstitials might have a significant mobility at low temperatures,¹ considerable effort has been spent both here and at other laboratories in the study of metals bombarded at low temperatures. As a function of time the bombardment temperatures have been getting progressively lower, and at present the lowest reported bombardment temperature is 3.8°K. These experiments have shown that some defect is indeed mobile at low temperatures, and in the case of aluminum and copper a significant annealing peak has been observed in the temperature interval from 30 to 50°K. The earliest interpretations assumed that this annealing peak was associated with a migration of interstitial atoms to vacant lattice sites. One of the most difficult problems arising in this interpretation lies in the fact that only about half the defects appear to be annihilated. Since equal numbers of vacancies and interstitials are created, it is difficult to imagine why only half of them would disappear if the above hypothesis were valid. The experiment discussed here was devoted to a study of the annealing kinetics in the region below 50°K. In particular, the experiments are designed to test the validity of interstitial migration and annihilation in this temperature interval.

Experimental Techniques

Bombardments were made in the Hole 12 cryostat of the ORNL Graphite Reactor. This facility, which incorporated a liquefier attachment, has been previously described.^{2,3} Bombardment temperatures were in the region between 3.8 and 4.2°K. Annealing was performed by locating the samples in a vacuum-tight can, together with a resistance heater. To pulse the samples, the

sample can was isolated from the wall of the cryostat and the heater utilized to heat the samples. The relatively low heat capacity at this temperature made it possible to raise the temperature of the samples as much as 30°K in a matter of a few seconds. The samples were rapidly quenched by injecting helium exchange gas into the space between the sample can and the cryostat wall. The time required to quench the sample 10 or 15°K was only a few seconds. By this technique both isothermal and isochronal anneals were made.

Isochronal anneals were made in the region from 4.2 to 40°K. It might be noted that the temperature was measured by means of a copper-constantan thermocouple. It is estimated that the temperature can be measured to about 0.5°K. Some difficulty is encountered in the measurements due to the presence of Thomson emf.

Results

The results of the isochronal annealing are shown in Figs. 24 and 25. Here we have plotted the resistivity recovery as a function of pulse temperature. The measurements were all at the base temperature of 3.8°K. It will be noted that in the first run (3-min pulses) for both aluminum and copper there was a dip at approximately 17°K, somewhat suggestive of the type reported by Walker and co-workers.⁴ The fact that both metals show the same dip makes it questionable that this is a real effect and, indeed, the subsequent measurements fail to show any such dip. Run 3 for both aluminum and copper (10-min pulses) is representative of the final points obtained during the study of isothermal annealing.

Isothermal annealing curves were obtained in approximately 2° intervals in the range from 9 to 20°K. The primary purpose of these experiments was to determine the activation energy utilizing the change in slope method suggested

¹H. B. Huntington, *Phys. Rev.* 91, 1092 (1953).

²R. R. Coltman, T. H. Blewitt, and T. S. Noggle, *Rev. Sci. Instr.* 28, 375 (1957).

³J. T. Howe, R. R. Coltman, and T. H. Blewitt, *Proc. 1957 Cryogenic Eng. Conf.*, p 173, 1957.

⁴J. W. Corbett and R. M. Walker, *Phys. Rev.* 110, 767 (1958).

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by Overhauser. At each temperature four points were determined. A typical plot of the isothermal annealing curves is shown in Fig. 26. It is estimated that the change in slope can be determined

Fig. 24. Isochronal Annealing of Copper Following 3.9°K Reactor Bombardment.

Fig. 25. Isochronal Annealing of Aluminum Following 3.9°K Reactor Bombardment.

to within a factor of 2. The computation of the activation energies from these data is shown in Table 3. The activation energies in the region between 30 and 50°K were also determined by the same method. The change in slope resulting when the temperature is raised from 36.2 to 38.9° is shown in Fig. 27. The activation energy in this temperature range was also determined utilizing the relaxation time method. This is done by measuring the time required to anneal out a given fraction of the resistance at two different temperatures. The results obtained to

Fig. 26. Isothermal Annealing of Copper at 13.5°K.

Table 3. Apparent Activation Energy for Cu and Al

Temperature Range (°K)	Al		Cu	
	ϵ (ev)	ϵ_{min} (ev)	ϵ (ev)	ϵ_{min} (ev)
8.5-11.2	0.020	0.020	0.022	0.019
11.2-13.5	0.032	0.032	0.035	0.031
13.5-14.5	0.054	0.049	0.040	0.039
14.5-15.7	0.049	0.049	0.065	0.065
15.7-16.75	0.081	0.069	0.080	0.068
16.75-17.8	0.077	0.070	0.095	0.088

Fig. 27. Isothermal Annealing of Irradiated Copper and Aluminum.

determine the activation energy by this method are shown in Fig. 28. The activation energies determined by both these techniques are shown in Table 4.

Discussion

The determination of the activation energies and of the isochronal annealing curves points out several interesting facts. First, it should be noted that annealing occurs at temperatures as low as 7.2°K. It would seem very difficult to ascribe this annealing to the same simple defect which is moved in the 30 to 50°K range. Some difficulty would, therefore, be expected in explaining the whole low-temperature annealing as the result of the motion of a simple defect. Second, it should be noted that the activation energies increase monotonically as a function of temperature. The discrete steps found by other investigators do not appear to be present here.⁴ It would thus seem difficult to apply the theory that close vacancy-interstitial pairs with discrete activation energies were present to account for low-temperature annealing. Finally, the magnitude of the activation energies seems

Fig. 28. Isothermal Annealing of Irradiated Copper and Aluminum at 36.2 and 38.9°K.

Table 4. Apparent Activation Energy for Recovery of Al and Cu at 36.2 and 38.9°K

Metal	Time at 38.9°K (min)	Time at 36.2°K (min)	ϵ (ev)
Cu	0.47	20.5	0.171
	0.97	59.7	0.186
	1.64	104	0.187
			0.164*
Al	0.408	11.4	0.150
	0.701	22.0	0.156
	1.32	43.5	0.158
	3.80	106.0	0.150
			0.153*

*From change in slope.

much too high to allow a simple process to be occurring. This is particularly noted when one calculates the number of jumps required for annihilation for any of the activation energies which have been determined. The results of such computations are shown in Table 5. For example, the activation energy of 0.187 eV found at 37°K for copper would require 10^{-10} jump. It is readily seen that this result is absurd, and one is forced to conclude that the rate equation cannot be applied to these results. At the moment the most feasible explanation would seem to lie in the fact that the activation energy is a spectrum, and the usual methods of determination of the activation energy of uniquely activated processes are not applicable.

IRRADIATION ANNEALING STUDIES OF VARIOUS METALS

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

In addition to the extensive low-temperature radiation-damage studies made on copper and aluminum, some annealing data has been obtained for a number of other metals. This data is in the form of isochronal annealing studies made after a bombardment of 4×10^{17} nvt at about 4°K, and the method used for temperature pulsing was the

Table 5. Average Number of Jumps Occuring Before Annihilation in the Case of Cu and Al*

Temperature (°K)	ϵ (eV)	Number of Jumps, n	
		Cu	Al
9.8	0.02	5×10^4	5×10^4
12.4	0.032	10^2	10^2
14.0	0.040	4	4×10^{-5}
15.1	0.065	5×10^{-6}	5×10^{-2}
16.2	0.080-0.068	1×10^{-9}	1×10^{-10}
17.2	0.095-0.088	2×10^{-12}	3×10^{-8}
37.4	0.180	2×10^{-10}	2×10^{-6}

*The values have been determined from the experimental activation energy and the rate equation; n is given by $\nu e^{-\epsilon/kT}$, where t is the time for annihilation, taken as 10^2 sec here, and ν is the atomic frequency factor, assumed to be 10^{13} .

same as that described in the section "Annealing Kinetics of Neutron-Irradiated Aluminum and Copper."

Figure 29 shows the isochronal annealing of high-purity zinc. Since the first point was obtained at 14°K, further study of zinc must be made to determine whether an annealing peak exists between 4 and 14°K or whether this recovery is the continuous type found in copper and aluminum in this temperature region. It may be noted that at about 50°K the beginning of a large recovery peak may be seen. This peak recovery had been observed earlier on specimens bombarded at 15°K.

Figure 30 shows the isochronal annealing of high-purity platinum. The large annealing peak shows about the same fractional recovery as that found in copper, but the peak is centered at about 20°K, whereas that of copper is at about 40°K.

Figure 31 shows the isochronal annealing of the noble metals. Silver behaves in much the same manner as copper except for a shift in the annealing to lower temperatures, the peak being centered at about 28°K. The similarity in recovery data between copper, aluminum, silver, and platinum is interesting with regard to both magnitude and general shape of the recovery curves. Although by no means conclusive, this similarity suggests that the distribution of defects after a low-temperature bombardment is somewhat the same in these four metals.

Fig. 29. Isochronal Annealing of Zinc.

Fig. 30. Isochronal Annealing of Platinum.

It can be seen in Fig. 31 that the isochronal annealing results for gold are completely anomalous with regard to the four metals listed in the previous paragraph. Although a small annealing peak may be present at 18°K, in general gold shows only continuous or "garbage"-type annealing. In view of the similarity of gold to copper and silver, this result is most surprising and is not understood at present.

In the previous progress report the fast-neutron damage rates (calculated from measured changes in residual resistivity at 4°K in the ORNL Graphite Reactor) of several metals were listed. During the past year additional measurements on other materials have been made. These results are shown in Table 6.

Fig. 31. Isochronal Annealing of Cu, Ag, and Au.

The total bombardment time over which measurements were made was about 150 hr in each case except for those materials listed in run HL-6, which lasted 65 hr. A 150-hr bombardment corresponds to an integrated fast flux of $4 \times 10^{17} \text{ nvt}$. None of the damage-production curves obtained for these materials showed indications of saturation. In the case of tin, it was possible to lower the sample temperature below the superconducting transition temperature of 3.73°K before and after bombardment when the reactor was off. During the experiment the tin was in the normal state. There was no change greater than a few tenths of a degree in the superconducting transition temperature. The same is true for lead and vanadium, which were bombarded in the superconducting state. In view of the relatively small bombardments used in these experiments and the known sensitivity of superconducting transition temperature to impurities, these results are not too

Table 6. Rates of Damage to Various Metals by Fast Neutrons at a Flux of 6×10^{11} neutrons·cm⁻²·sec⁻¹ in Hole 12 of the Graphite Reactor

Specimen	Residual Resistivity Before Bombardment ρ_0 (ohm-cm)	Damage Rate dp/dt (ohm-cm/hr)	Bombardment Temperature (°K)	Run
Copper	6.2×10^{-10}	2.46×10^{-11}	4.17	HL-2
Copper (cold worked)	4.8×10^{-8}	3.35×10^{-11}	4.17	HL-2
Gold	3.5×10^{-8}	3.02×10^{-11}	4.06	HL-4
Tin	5.4×10^{-8}	$\sim 4.4 \times 10^{-11}$ *	4.06	HL-4
Silver	2.0×10^{-9}	5.15×10^{-11}	4.06	HL-4
Platinum	1.4×10^{-7}	6.60×10^{-11}	4.17	HL-2
Aluminum	4.0×10^{-9}	8.43×10^{-11}	3.9	HL-5
Nickel	2.2×10^{-8}	1.33×10^{-10}	4.2	HL-6
Iron	8.6×10^{-7}	$\sim 1.6 \times 10^{-10}$	4.3	HL-1
Zinc	4.5×10^{-9}	2.13×10^{-10}	4.17	HL-2
Magnesium	3.9×10^{-8}	2.55×10^{-10}	4.2	HL-6
Bismuth	1.7×10^{-5}	2.28×10^{-7}	4.2	HL-6

*Single crystal.

surprising. It may be noted in Table 6 that for many materials the damage-induced change in resistivity after 150 hr is greater than the initial residual resistivity. The damage rates listed in Table 6 are arranged in increasing order, and it can be seen that high-purity bismuth is damaged 10^4 times as fast as copper. Since bismuth has a very low carrier concentration, this result clearly points out the importance of this parameter in correlating neutron damage rates in different materials.

THE EFFECT OF ANNEALING IN OXYGEN ON THE RESIDUAL RESISTIVITY OF COPPER

J. K. Redman R. R. Coltman
T. H. Blewitt C. E. Klabunde

During the past year work was continued on the study of the effects of annealing in oxygen on the residual resistivity of nominally high-purity (ASR 99.999%) copper. Earlier work reported by the group^{5,6} has shown that the residual resistivity of copper can be reduced by as much as a factor of 20 by annealing in a poor vacuum (20 μ air) at 900°C. More recent quantitative data

shows the decay of residual resistivity as a function of annealing time in air. All electrical measurements have been made on copper single crystals in a bath of liquid helium (4.2°K) following pulse anneals for various times in a poor vacuum of about 30 μ of air. Figure 32 shows the decay of resistivity of a specimen whose initial residual resistivity was somewhat high. The annealing conditions were 700°C and 30 μ of air. For this specimen the residual resistivity decreased by a factor of 50. Figure 33 shows the decay curves of two other samples with different values of initial residual resistivity. The initial resistivity of sample 476-A was 4×10^{-9} ohm-cm, saturating at 9×10^{-10} ohm-cm, and the initial value of sample 475-F was 2.1×10^{-9} ohm-cm, saturating at 4.8×10^{-10} ohm-cm.

It has been found that there is no effect when specimens are annealed in a poor vacuum of pure nitrogen, hence it is certain that oxygen causes

⁵T. H. Blewitt *et al.*, *Solid State Ann. Prog. Rep.* Aug. 31, 1958, ORNL-2614, p 65.

⁶J. K. Redman *et al.*, *Bull. Am. Phys. Soc.* 4, 150 (1959).

Fig. 32. The Effect of Annealing at 700°C in 30 Microns of Air on the Residual Resistivity of Copper.

the changes. It has also been found that annealing in chlorine will reduce the residual resistivity. For example, a 15-min anneal at 980°C in 10 μ of Cl_2 reduced the resistivity of a copper crystal by a factor of 5. Furthermore, annealing at high temperatures in reducing atmospheres (hard vacuum with the specimen in contact with graphite, hydrogen, or carbon monoxide) can restore the residual resistivity of an air-annealed specimen to near its original value. The process seems to be completely reversible but requires somewhat higher temperatures for a reducing treatment than for an oxidizing treatment.

The precise mechanism by which the resistivity is lowered upon annealing in oxygen is not understood. Because of the small amount of impurity present in the copper, it seems difficult to believe that precipitation is induced by the oxidizing treatment. It does seem possible that the simple oxidation of impurities might decrease their scattering cross section. This might be particularly true of iron as an impurity; it is known to have an anomalously high scattering cross section in the metallic state in copper.

It has also been found that an oxidizing or reducing heat treatment of high-purity copper also affects the temperature dependence of resistivity in the region of 2–20°K. This is discussed in

Fig. 33. The Effect of Annealing at 700°C in 30 Microns of Air on the Residual Resistivity of Copper Single Crystals.

more detail in the section "The Resistance Minimum and Resistivity of Copper at Low Temperatures."

STORED ENERGY OF IRRADIATED COPPER

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

A redetermination of the stored-energy release in reactor-irradiated copper between 30 and 50°K was made under much more favorable conditions with new refinements of the nuclear-heating calorimetry method. The result, 0.19 cal/mole for 4×10^{17} *nvt*, confirms earlier figures with a much higher certainty. This reconfirms the difficulty of explaining the 30–50°K peak in annealing of radiation-induced resistivity on the basis of simple interstitial-vacancy recombination. A more detailed report has been published.⁷

⁷T. H. Blewitt, R. R. Coltman, and C. E. Klabunde, *Phys. Rev. Letters* 3, 132 (1959).

DESIGN OF A NEW LOW-TEMPERATURE IN-PILE FACILITY WITH A NEUTRON CONVERTER

J. Diehl⁸ T. H. Blewitt
R. R. Coltman

So far all experiments concerning radiation damage due to neutron irradiation at very low temperatures have been carried out in the helium cryostat,⁹ located in Hole 12 of the Graphite Reactor. At present a new low-temperature facility, which will be placed in Hole 10 of the same reactor, is under construction. In principle the new cryostat is similar to the Hole 12 cryostat; however, it will incorporate a tube of a uranium-aluminum alloy highly enriched with U²³⁵, which will convert the majority of the thermal neutrons into high-energy fission neutrons. A low-temperature facility with a neutron spectrum changed in such a manner seemed to be desirable for two reasons: (1) since the radiation damage in metals is primarily due to fast neutrons, a converter enhances the rate of damage considerably and therefore allows investigations involving higher total changes in the physical properties of the samples during comparable irradiation times; (2) comparative studies in facilities with and without a converter should provide some valuable information about the influence of the neutron spectrum on the details of radiation-damage effects. In the following, the design of the converter and the cryostat will be described briefly.

The water-cooled converter and the cryostat are built up essentially of six coaxial aluminum tubes, about 22 ft long (see Fig. 34). At the outside, tube No. 2 is connected at its lower end with the converter tube, which is an aluminum-clad cylinder of a uranium-aluminum alloy containing 43 wt % of highly enriched uranium. The U-Al core is 1 ft long with a wall thickness of $\frac{3}{32}$ in. The cooling water flows through the annuli between tubes Nos. 1 and 2 and between Nos. 2 and 3. It carries away the heat developed by the fission process in the converter, which has been calculated to be at most about 1.8 kw. The water intake and outlet

lines will be connected to an existing demineralized-water circuit which is used for the cooling of the Hole 51 converter.

The main part of the cryostat itself consists of the three inner tubes (Nos. 4, 5, and 6). Its design is somewhat different from that of the Hole 12 cryostat, and is essentially simplified, partly because of the stronger limitations in space due to the converter tube, and partly as a consequence of the experiments made with the old cryostat. The main difference is that the new cryostat does not contain a special heat exchanger around the sample tube. The aluminum sample tube (No. 6) will be cooled by the cold helium gas (which will be supplied by the same expansion-engine refrigerator that operates the Hole 12 cryostat) streaming down between tubes Nos. 5 and 6. After reversing flow at the end of tube No. 5, the gas returns through the annulus between tubes Nos. 4 and 5. As in the old cryostat, static exchange gas in the sample tube will provide the heat contact between the cold wall of the sample tube and the samples themselves. This gas can be pumped out to insulate the samples thermally during annealing experiments. High vacuum between tubes Nos. 3 and 4 will provide the thermal insulation between the cryostat part and the converter section. Since the flange at the upper end of the sample tube stays at room temperature, a heat trap consisting of a 1-ft-long section of thin-walled stainless steel tubing is inserted between the upper end of tube No. 6 and that flange. The procedure for making the joint between aluminum and stainless steel has been described.⁹ Similar joints are used in the helium intake and outlet lines. No special provisions have been necessary to allow for different thermal expansions in different parts of the cryostat. The cold tubes are connected with each other and with the rest of the assembly only at the top and are otherwise free to slide along each other in an axial direction. In case of any failure, the cryostat can be pulled out of the converter tube after opening the main flange around the outermost tube, so that it would not be necessary to remove the converter from the pile.

Under some simplifying assumptions, the thickness of the converter tube was determined in such a way that the number of fissions per unit time should be more than 90% of the maximum number obtainable with a completely "black" cylinder having the same outer diameter. If one assumes

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⁹R. R. Coltman, T. H. Blewitt, and T. S. Noggle, *Rev. Sci. Instr.* 28, 375 (1957).

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Fig. 34. Schematic Diagram of Hole 10 Cryostat.

that the damage, that is, the number of defects produced by fast neutrons in a metal, is proportional to the neutron energy E , then the damage rate inside the converter should be increased by approximately a factor of 6. By taking into account the attenuation of the fast neutrons in the water jacket around the converter, this factor will be reduced to about 5. Only a very rough estimate has been made of the increase in gamma heating due to the converter. Since this estimate shows the increase will be smaller than a factor of 2, it should not cause any serious difficulty.

DETERMINATION OF THE GAMMA FLUX AND NEUTRON FLUX IN THE POOL OF THE ORR

T. H. Blewitt J. Diehl¹⁰

Introduction

A facility was built in the pool of the Oak Ridge Research Reactor opposite fuel position A-4 for the preliminary purpose of determining the nuclear heating and the neutron flux in the proposed location of a cryogenic loop. These two pieces of data are essential in evaluating the usefulness of a low-temperature bombardment facility and in constructing it.

The large value of the nuclear heating expected in a water-moderated reactor, such as the ORR, will play a very important part in the final design of the cryostat since limited amounts of refrigeration are available. The data determined from this experiment indicated that sufficient refrigeration was available to construct a cryostat of useful size with an operating temperature of 20°K. The neutron flux measurements, however, indicated that a sufficiently high damage rate was not available to warrant construction of such a cryostat if an enriched graphite reactor were available.

Construction of Facility

The bombardment facility at the ORR pool is essentially an aluminum U-tube. In order to reduce neutron moderation to a minimum, a box filled with helium gas was built around the U-tube to occupy the volume between the tube and the reactor face. It is estimated that only $\frac{1}{8}$ in. of water lies between the sample and the reactor

tank. Samples are inserted through a Wilson seal located at a thimble at the tank wall. Cooling is provided by the circulation of helium gas at a rate of 20 cfm at a pressure of 50 psi. A Carrier F-20 hermetically sealed compressor is utilized as the circulator. An after-cooler is provided to prevent excessive oil carry-over at the discharge end of the compressor. Micro Metallic filters are located in the discharge side of the circuit so that dust is trapped before it enters the pool and becomes radioactive. A Micro Metallic filter is also provided on the inlet side of the compressor so that any radioactive particles will be trapped before they enter the compressor.

Rupture disks are located in various places to prevent bursting of the pipes. In the event of a rupture the gas will be discharged into the radioactive off-gas line. In addition to the cooling system, a high-speed vacuum system consisting of a Kinney mechanical pump and an oil diffusion pump is provided so that samples can be isolated by evacuating the tube.

Determination of the Gamma-Ray Heating

Gamma-ray heating measurements have been made at the ORNL Graphite Reactor by determining the time-temperature curve for a sample of copper in the region from 20 to 50°K. In this reactor the low-temperature measurements are essential since the gamma heating is relatively small, so that radiation losses must be reduced by the utilization of low temperatures. At room temperature the effect of thermal radiation would be sufficiently great to introduce considerable error into a gamma-ray heating measurement.

The problem, however, at the ORR is considerably different, since the gamma-ray heating is several orders of magnitude greater than that in the Graphite Reactor. Accordingly, the measurements of the nuclear heating were made by determining a time-temperature curve above room temperature. A sample of copper was carefully polished and suspended in the U-tube by means of a copper constantan thermocouple approximately 2 ft from the center of the reactor. The U-tube was evacuated and the reactor stabilized at 4 Mw. The sample was pushed into the center line of the reactor, where it received the maximum intensity of nuclear heating, a Wilson seal was used to maintain the high vacuum, and the temperature was determined as a function of time. From the known value of

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the specific heat of copper the rate of heat input can be determined. Similar measurements were also made at 8 Mw of reactor power. The results are shown in Figs. 35 and 36. Computations of the gamma-ray heating with a correction for radiation losses (thermal radiation effects are about one-fifth of the gamma-ray heating at 8 Mw of reactor power and a sample temperature of about 350°C) indicate that gamma-ray heating is 0.7 w/g at a full operating level of 20 Mw.

Determination of the Neutron Flux

For the purpose of radiation damage studies the change in electrical resistance and the flow stress

Fig. 35. Time-Temperature Curve at 4 Mw Reactor Power.

Fig. 36. Time-Temperature Curve at 8 Mw Reactor Power.

are excellent neutron dosimeters. In the past a fairly comprehensive study of the effect of neutron irradiation on the flow stress and the room temperature resistivity of copper has been made. Some of the results of these studies are shown in Fig. 37.

All measurements are made in reference to the neutron spectrum which occurs in a uranium donut in the center of the Graphite Reactor. In essence, the neutron spectrum is a $1/E$ spectrum with the thermal neutrons converted to fission neutrons. It has been found that insofar as the flow stress and the electrical resistance are concerned the neutron converter enhances the damage rate by a factor of 5. As a result, if it is desired to convert the results of Fig. 37 to a location in which a pure $1/E$ spectrum appears, the neutron dose should be multiplied by a factor of 5. On the basis of a change in flow stress of a copper single crystal bombarded in the ORR facility described above, a three-week bombardment was equivalent to 1.5×10^{19} nvt. A similar figure was reached when the change in resistance was considered. It thus turns out that the neutron flux is equivalent to 1×10^{13} neutrons·cm⁻²·sec⁻¹. In reference to a $1/E$ distribution, the neutron flux is equivalent to 5×10^{13} neutrons·cm⁻²·sec⁻¹.

Conclusions

The facility constructed to measure the neutron flux and gamma heating turns out to be a very useful one for the bombardment of samples near 50°C. This is true because of its relatively high flux and carefully controlled temperatures. In addition, the high gamma flux makes it feasible

Fig. 37. Dose Dependence of the Critical Shear Stress of Copper Single Crystals as Used for Calibrating the Neutron Flux in the ORR Facility.

to use this facility to measure specific heats and associated measurements, for example, stored energy in the range of 50 to 600°C since the heat input is large in comparison to the radiation losses at these temperatures.

It does not, however, appear that this facility would be particularly advantageous for the construction of a high-flux (damage rate) cryostat. The major difficulty arises from a high gamma heat per neutron, which is of course a consequence of water moderation (for example, the gamma heat per neutron is generally an order of magnitude larger for a water-moderated reactor than for a graphite-moderated reactor), and from the neutrons from a relatively large solid angle being considerably moderated by the poolside water. This latter factor is a consequence of the reactor face being stepped 8 in. from the reactor tank. The net effect then of these factors is to increase the gamma flux by a factor of 200 over that now existing in the Graphite Reactor, while the damage rate is enhanced by a factor of 50 over that in the existing Hole 12 cryostat (in the Graphite Reactor). In both cases considerable improvement in the ratio of the gamma flux to the damage rate would result if a fission spectrum were employed. This could be done in the ORR by moving the sample to the reactor face (unfortunately for practical purposes the step in the tank prohibits the location of the cryostat in this position). In the case of the Graphite Reactor the damage rate could easily be enhanced by a factor of 5 by the use of a converter with only a small enhancement of the gamma-ray heating. The most favorable conditions for the construction of a cryostat would occur under the proposed enhancement of the Graphite Reactor. In this case the thermal flux would increase by a factor of 5, so that by using a converter the damage could be enhanced by a factor of 25 over that now observed in Hole 12. At the same time the gamma flux would be expected to increase by no more than a factor of 6. Hence, a damage rate only a factor of 4 down from that in the ORR poolside facility should result with a gamma heating which is down by a factor of about 50. However, while by no means the ideal situation, it is possible to design and operate with the refrigeration now available at ORNL a cryostat in the pool of the ORR provided that adequate space for direct access to the sample chamber is made available.

THE RESISTANCE MINIMUM AND RESISTIVITY OF COPPER AT LOW TEMPERATURES

S. T. Sekula

The existence of an electrical resistance minimum in copper has been ascribed by some workers¹¹ to the presence of small concentrations of specific metallic solutes in the metal, while others¹² have suggested structural defects in the metal as playing a major role. Recently Redman *et al.*¹³ demonstrated that the resistivity of single crystals of copper is markedly dependent on their thermal history. In particular, the resistivity at the normal boiling point of helium was found to decrease with increasing exposure time in an annealing treatment at 700°C in 30 μ of air and to attain a constant value after 5 hr of heat treatment. A re-examination of the earlier work¹² on the resistance minimum in copper in light of these new data suggested the possibility that the resistance minimum was influenced by the hardness of the vacuum during the annealing treatment. MacDonald and Pearson¹¹ also observed that the anomalous resistivity minimum seemed strongly dependent on reducing or oxidizing atmospheres during the melting of copper. A study of the role of the annealing atmosphere on the electrical resistivity minimum of copper was therefore felt to be of considerable interest.

The experimental techniques for these measurements are sketched briefly here, with a detailed description reserved for later publication. The samples consisted of 0.05-cm-dia copper wire 25 cm in length wound around a quartz tube. The specimens were annealed in an evacuated mullite tube which allowed for annealing in desired atmospheres by means of a controlled leak. The resistance measurements were made on a Wenner potentiometer. Provisions for pumping on the helium bath and a heater coil around the thermometer bulb which also served as a sample container enabled a temperature range to be covered from 1.7 to 25.0°K.

¹¹D. K. C. MacDonald and W. B. Pearson, *Acta Met.* 3, 392 (1955)

¹²T. H. Blewitt, R. R. Coltman, and J. K. Redman, *Phys. Rev.* 93, 891 (1954).

¹³J. K. Redman *et al.*, *Bull. Am. Phys. Soc.* [2]4, 150 (1959).

One particular sample of copper was subjected to 11 heat treatments in alternate oxidizing and reducing atmospheres. In every case annealing in a reducing atmosphere increased the over-all resistivity and brought on a resistance minimum. Annealing in an oxidizing atmosphere reduced the resistivity and washed out the minimum. Curve 1 of Fig. 38, which is typical after a reducing treatment, was obtained by annealing the sample in a graphite boat in a vacuum of 2×10^{-5} mm Hg. A resistance minimum is found at about 12.5°K and an abrupt increase in the resistivity is seen in the region from 6 to 8°K. The sharp rise was found to be due to the method of attaching electrical contacts to the sample and is incidental to the appearance of the resistance minimum. A typical curve following an air anneal (10μ at 750°C for 2 hr) is shown in curve 2 of Fig. 38. The resistivity at 4.2°K has decreased by approximately a factor of 5 and the minimum is not observable. An activation analysis revealed the presence of iron as the major impurity and smaller amounts of silver and zinc. Unfortunately it was not possible to obtain numerical values for these concentrations.

Fig. 38. Temperature Dependence of the Resistivity of Copper with a Small Impurity Content After Annealing in a Reducing Atmosphere and an Oxidizing Atmosphere.

Similar results were found in a copper sample of much higher purity. In this case the specimen was annealed in a vacuum of 2×10^{-5} mm Hg at 950°C for 2 hr and was found to have a resistance minimum as shown in Fig. 39. It should be noted that the low resistivity of this sample following the treatment in a reducing atmosphere is an indication of high purity. The results upon reheating this specimen in 10μ of air at 750°C for 2 hr are also shown in Fig. 39. The resistivity minimum is no longer observed and the residual resistivity is seen to have decreased approximately by a factor of 3.

These results, while not completely understood, indicate the strong influence of trace impurities on the residual resistance and the resistance minimum of copper at low temperatures. It is particularly significant in this regard that the anomalous resistivity minimum is reversible and can be introduced or removed at will by a heat treatment in an appropriate atmosphere. These results would then seem to clearly show that the resistance minimum is not a fundamental property

Fig. 39. Temperature Dependence of the Resistivity of 99.999% Pure Copper (American Smelting and Refining) After Annealing in a Reducing Atmosphere and an Oxidizing Atmosphere.

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of the copper but a manifestation of the state in which trace impurity atoms are present in the copper. Moreover, these results suggest that the many conflicting observations on the resistance minimum may be due to differences in the preparation of the samples.

In addition to work now in progress with dilute alloys of copper with various impurities subjected to oxidizing and reducing atmospheres, a similar study is contemplated for silver and gold. The effect of other reducing atmospheres on the resistivity of copper is also under investigation.

ELECTRON MICROSCOPE STUDIES

T. S. Noggle

J. O. Stiegler

FISSION FRAGMENT TRACKS IN UO_2 FILMS

Direct electron microscope examination of thin films of UO_2 irradiated with thermal neutrons has revealed a random system of lines and spots which may be interpreted as tracks left by fission fragments produced in the films.¹ In this study films of approximately 100 Å thickness were prepared by the vacuum evaporation of U_3O_8 . Prior to irradiation the films are structureless; afterward, track patterns such as the one shown in Fig. 40 are always observed, with the density of tracks proportional to the time of irradiation. The contrast effect does not change significantly enough to either identify the point along a track where the fission event occurred or distinguish which class of fragments, light or heavy, is responsible for a given length of track; however, the observed distribution of lengths can readily be explained in terms of the projections of a random distribution of fission fragment trajectories onto a plane surface.

Replication of free surfaces of these films has established that the contrast effect observed along the path length arises principally from local changes in the film thickness resulting from the

passage of a fission fragment through the film. Figure 41 is a micrograph from a replica of the free surface of a UO_2 film irradiated in place on the substrate upon which it had been formed. The structure seen here arises only from the topography of the surface and for the long track is interpreted as a furrow 50 to 100 Å wide, of uncertain depth but less than the film thickness (100 Å). The material displaced from the furrow appears as small irregular clumps on both sides of the furrow. The scattering of spots present in Fig. 41 represents material present as small clumps on the surface and/or local bulging. These observations indicate that the type of radiation effect observed here is a manifestation of the passage of fission fragments through the solid near the surface and, as such, represents a special case of radiation damage.

Measurements on the density of the observed structure indicate that to within a factor of 2 there is a direct correspondence between the observed density and the expected frequency of fission events in the film. Further work in which the thermal flux is carefully monitored is necessary before a more exact estimate of the fraction of fission events observed by this technique may be made. Measurements on the distribution of track lengths give results which agree within the

¹J. O. Stiegler and T. S. Noggle, *Bull. Am. Phys. Soc.* [2]4, 141 (1959).

Fig. 40. Transmission Electron Micrograph of Fission Fragment Tracks Produced in a 100-Å-Thick Film of Uranium Dioxide During Neutron Irradiation of $\sim 5 \times 10^{15}$ nvt. 25,000X. Reduced 38.5%.

Fig. 41. Electron Micrograph of a Carbon Replica Taken from the Surface of a Thin Film of Uranium Dioxide Following Irradiation of $\sim 5 \times 10^{15}$ nvt. 80,000X. Reduced 38%.

probable error of the measurements with the distribution expected from simple geometric considerations; however, no tracks longer than $5\ \mu$ have been observed, which indicates that nuclear scattering events may affect the distribution of the longer tracks.

Occasionally the longer tracks are bent (Fig. 42), presumably as a result of the direct interaction of the fission fragment with a lattice atom in which a relatively large amount of energy is transferred to the lattice atom. In most of these cases it is not possible to detect a track which may be ascribed to the path of the ejected atom; however, in a few cases, forking of the tracks has been noted and the angles made by the tracks have been measured. An analysis of the mechanics of the system in which an energetic fission fragment interacts with a lattice atom indicated that fission fragments of mass numbers 80 to 95 have interacted with oxygen atoms in the lattice.

The general absence of forking with these bent tracks (see Fig. 42) raises a question as to the conditions necessary for the registration of a track in these films. A qualitative insight is obtained from theoretical estimates of the energy loss of an energetic particle per unit length of path. The estimated rate of energy loss for a fission fragment is about $1000\ \text{ev}/\text{\AA}$ initially, decreasing to about $50\ \text{ev}/\text{\AA}$ at 90% of its range. An oxygen atom ejected from a lattice site under conditions of maximum energy transfer with the more energetic fission fragments would initially lose energy at a rate of about $200\ \text{ev}/\text{\AA}$. The

Fig. 42. Electron Micrograph of a Bent Track Produced by the Interaction of a Fission Fragment and a Lattice Atom. 70,000X. Reduced 38%.

1.5- to 2-Mev alpha particles would initially lose energy at a rate of about $25\ \text{ev}/\text{\AA}$. The alpha particle results are of interest since specimen preparations of UO_2 depleted in U^{235} with Li^6 or B^{10} evaporated onto the surface have failed to show the tracks which might be expected from the alpha particles produced by the reactions of these isotopes with neutrons. These observations indicate that an energy input to the UO_2 films along the path of an energetic particle of $25\ \text{ev}/\text{\AA}$ does not give rise to sufficient changes in the films to be detected under the present conditions of observation. The occasional observation of forked tracks indicates that an energy input of less than $200\ \text{ev}/\text{\AA}$ will register.

The observations to date have not indicated the presence of radiation effects other than the surface disturbances noted. It is possible that there are structural changes occurring in the vicinity of the fission fragment paths which at present are not recognized or detected. Additional work, particularly with respect to specimen preparation techniques, is needed to evaluate the prospects of studying other radiation effects which might be present. Work in progress is currently directed at improving the statistics both for track densities and the distribution of track lengths for correlation with the theoretically expected values.

RADIATION EFFECTS IN GOLD FILMS

The examination of thin, single-crystal gold films after reactor irradiation has shown the presence of a structure that was introduced by the irradiation.² Figures 43a and 43b show the same area of a film before and after irradiation, the faint ring-like spots present in Fig. 43b being observed only after irradiation and believed to be due to the interaction of fast neutrons with the gold films. The apparent diameter of these rings is approximately $100\ \text{\AA}$. The density of this structure varies directly with the fast-neutron dose, for $5 \times 10^{17}\ \text{nvt}$ being about 5×10^{15} per cubic centimeter. This density corresponds to about 1% of the expected knock-ons in which a neutron transfers energy in excess of 1000 ev to a lattice atom. Thus, if this structure is developed directly by the neutron hits, it must be only the most energetic hits which give rise to changes which lead to the present observations.

²T. S. Noggle, *Bull. Am. Phys. Soc.* [2]4, 137 (1959).

Fig. 43. Transmission Electron Micrograph of 300-Å-Thick, [100] Oriented Gold Films. (a) Before irradiation, (b) after 5×10^{17} nvt fast neutrons. 100,000X.

On the other hand, this structure may develop by the aggregation of mobile point defects produced by the irradiation. In this case, the uniformity in the size and appearance for different irradiation doses indicates that the aggregates must grow to some limiting size, and the dose dependence of the density indicates that the nucleation of the aggregate is directly related to the dose. Finally, it has not been established whether this structure is developed during the irradiation or whether it represents some aspect of annealing which might occur in areas illuminated by the electron beam during examination in the microscope.

The variation in appearance of this structure with variation of the diffraction conditions suggests that this is a structural defect which manifests itself by local perturbation of the diffraction process.

The principal source of contrast in crystalline materials examined in the electron microscope arises from diffraction effects. In general, diffraction will subtract intensity from the primary beam so that with the normal apertures employed the diffracted rays will be intercepted by the apertures and will not contribute their intensity to the

final image. Thus, the regions which are most accurately oriented for diffraction to occur will appear essentially opaque in the electron image, while areas oriented so that little diffraction occurs will appear quite transparent. Structural defects such as dislocations, twins, or stacking faults are observable as a result of the local changes in the diffraction that they produce as a result of strains, changes in orientation, or phase shifts in the transmitted and diffracted rays. With the thin film preparations studied here, it is unavoidable that flexing of the films occurs; consequently, in general the range of orientations present over areas a few microns in extent will give rise to cross grating diffraction patterns in which the individual spots will be predominantly produced by small local regions in the films. These changes in local diffraction intensity and diffraction order as a result of slight orientation changes give light and dark regions in the microscope image.

Systematic investigation of the interrelation between appearance and diffraction requires a precision of specimen manipulation which is not currently available. Other observations on replicas

of the film surfaces and on annealed films containing small voids less than $100 \text{ \AA}$ in diameter indicate that we are probably not dealing with surface phenomena or with voids in the films. Some similarities may be noted between the structure observed here and some of the structures that are developed by quenching from high temperature.³ This suggests that we are dealing with collapsed disks of vacancies as in the case of quenched metals; however, an interpretation such as this must be considered as only speculative at the present time.

REPLICATION OF COPPER SURFACES

The work carried out for the Surface Group on some of their copper specimens, as well as the preliminary observations on the surface structures of deformed copper, has indicated the need for an improved technique for replication of the surface of copper. The requirements of both studies call for high-resolution replica techniques which essentially limit the replica material to evaporated films. In addition, it is desirable that a pre-shadowing technique be employed in order to facilitate control over the shadowing direction relative to the surface. The most critical stage in replication with evaporated films is the stripping process, which is usually effected by use of acid attack to undermine and free the evaporated films. In addition to extensive etching of the surface, this method is somewhat erratic in the ease with which it frees the films, and too frequently the gas evolved by the etching process breaks up and disperses the films into unusable fragments. The method described below relates primarily to a stripping method which substantially overcomes the drawbacks of stripping with acid and was evolved in good part from the experience of the Surface Group on the surface reactions on copper.

The present method normally involves the pre-shadowing of the specimen surface with platinum, followed by the forming of a carbon film by evaporation — both of these steps being carried out in a vacuum of 10^{-4} to 10^{-5} mm Hg. Subsequent to the forming of the carbon film, the specimen is held for 5 to 10 sec in the fumes above a partially filled container of concentrated nitric acid. It is

then slowly immersed into a 0.1% solution of ethylenediamine (1 cc of 98% ethylenediamine per liter of water). The replica will float free onto the solution, can be transferred to distilled water baths for washing, and then can be picked up onto specimen grids for examination in the microscope.

The stripping action of the ethylenediamine is believed to occur as a result of dissolution of copper oxide on the surface of the copper and involves chemical reactions similar to those discussed by the Surface Group in this report. The copper oxide layer normally present on the specimens in itself usually does not permit stripping to occur; hence the exposure to the fumes of nitric acid is an essential step in the procedure. It is thought that the thin carbon film acts as a permeable membrane to the oxidizing constituents in the nitric acid fumes, permitting further oxidation under the replica layer. In support of this, it has been noted that the thinner the carbon film, the more reliably and rapidly it may be removed in the ethylenediamine solution. In addition, films thicker than an estimated $300 \text{ \AA}$ are not readily removed by this technique.

This method is being employed in the study of the effect of reactor irradiation on the deformation of copper. Figures 44 and 45 illustrate the striking changes which occur as a result of irradiation. Figure 45 is perhaps an extreme example but does show the very large slip steps which may be encountered in the irradiated specimens. Figure 46 is an example showing the possibility of

Fig. 44. Slip Lines on Single-Crystal Copper Specimen Deformed in Tension to 10% Elongation. Reduced 38%.

³P. B. Hirsch and J. Silcox, *Growth and Perfection of Crystals*, p 262, Wiley, New York, 1958.

repeated replication of the same surface. In this case, the general roughening of the surface and frequent coarse pitting produced by the two preceding replications are apparent; however, the original slip lines are still well defined and, in addition, may be differentiated from those intro-

duced by the last strain increment since the slipped surface of the original lines has been slightly roughened as a result of the prior replication.

Fig. 45. Slip Lines on Irradiated Single-Crystal Copper Specimen Deformed in Tension to 2% Elongation. The deformation was concentrated in one region of the specimen; so the local deformation level is 5 to 10 times greater, i.e., 10–20% elongation. Irradiated to $\sim 10^{19}$ *nvt* fast neutrons. 10,000X. Reduced 38%.

Fig. 46. Slip Lines on Irradiated Single-Crystal Copper Specimen Deformed in Tension. Specimen deformed to 5% extension, electropolished, and strained an additional 2%, and the surface replicated twice. It was then given an additional 1% extension and then replicated again. This micrograph is from the final replica and illustrates the effect of previous replications on the surface. Irradiated to $\sim 10^{18}$ *nvt* fast neutrons. 10,000X. Reduced 35%.

CHEMICAL PROPERTIES OF METAL SURFACES

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DISSOLUTION OF COPPER IN
AQUEOUS ETHYLENEDIAMINE

When single crystals of copper are exposed to aqueous solutions which contain reagents capable of oxidizing and dissolving copper, facets and/or pits are developed on the surface of the crystal. The geometrical symmetry of these facets or pits is a function of, among other things, the crystallographic orientation of the exposed face of the metal crystal. It is generally believed that some of the pits and facets in the surface should bear a relationship to points where dislocations in the crystal intersect the surface, since these are the points at which the chemical potential is greater than that of an idealized atomically smooth surface. Kinks, steps, and other points of departure from the theoretically ideal surface should also be energetically more favorable as sites where reactions are initiated. To test these ideas, a program to investigate the dissolution of copper in aqueous solutions has been initiated. The data reported here were obtained from the reaction of copper with oxygen dissolved in dilute aqueous solutions of ethylenediamine. The over-all reaction is described by the following equation:

Experimental Procedure

Oriented single crystals of 99.999% copper grown by the Bridgman technique, $0.1 \times 1 \times 2$ cm, were polished by the method of Young *et al.*¹ and suspended from the hook in the glass reaction apparatus shown in Fig. 47. About 82 ml of 10^{-2} m aqueous ethylenediamine saturated with air was introduced into the volumetric bulb and this solution sealed from the remainder of the system by closing the proper stopcocks. The apparatus was connected to a hydrogen-vacuum system and flushed with purified hydrogen until all detectable traces of oxygen were removed. The copper sample was then annealed under hydrogen at 450°C for 16 hr, after which the apparatus was closed and placed in a water bath controlled to $\pm 0.02^\circ\text{C}$. When temperature equilibrium had been established, the solution was allowed to flow

from the volumetric bulb into the reaction chamber. The course of the reaction was followed by measuring the conductivity changes in the solution, which was stirred with a magnetic stirrer, as a function of time. Since excess ethylenediamine was present, the extent of the reaction was governed by the amount of oxygen contained in the solution.

The relative concentration of a component which determines the extent of a reaction may be expressed as a function of the conductivity values of the solution:

$$\% \text{ material unreacted} = \left(1 - \frac{\Delta\sigma_t}{\Delta\sigma_f} \right) 100, \quad (2)$$

where $\Delta\sigma_t$ = conductivity change from time zero

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Fig. 47. Portion of Filling Rack with Reaction Chamber.

¹F. W. Young, Jr., J. V. Cathcart, and A. T. Gwathmey, *Acta Met.* 4, 145 (1956).

to time t and $\Delta\sigma_f$ = conductivity change from time zero to time reaction completed. If observed resistance values are substituted for conductivity values in the first-order rate equation, the expression becomes

$$\log \frac{R_f - R_i}{R_i} + \log \frac{R_t}{R_f - R_t} = \frac{kt}{2.303} \quad (3)$$

where R = observed resistance of the solution and the subscripts i , t , and f refer to the initial value before reaction has commenced, the value at time t , and the final value at the completion of the reaction, respectively. A plot of $\log [R_t/(R_f - R_t)]$ vs time should give a straight line, the slope of which is equal to $k/2.303$, if first-order kinetics are obeyed.

For such a treatment it is not necessary that the concentrations of the components be known, but at the completion of the reactions the solutions were analyzed for copper by the neocuproine method of Smith and McCurdy.² Data on the solubility of air in water³ agreed with the copper analysis and showed that the extent of the reaction was limited by the amount of oxygen dissolved in the solutions.

Rate data were given at three different stirring speeds at temperatures of 7.50, 25.00, 34.55, 47.04, and 56.57°C (all $\pm 0.02^\circ\text{C}$).

Replicas of many crystal surfaces were made in order to determine the changes produced by the reaction. Samples whose surfaces were replicated were not always allowed to react to completion but were removed from the reaction vessel after the desired amount of copper had been removed. The crystal was washed in a stream of distilled water for 1 min and then dried in a stream of oxygen. Surfaces were replicated with carbon preshadowed with platinum at a 4:1 shadow angle.

Experimental Results

Rate Data. — Rate data were gathered principally on the (111), (100), and (110) faces of copper crystals. Kinetic results were the same for all faces, and the data discussed below and shown in the illustrations are representative since no exceptional behavior was noted in any case.

²G. F. Smith and W. H. McCurdy, Jr., *Anal. Chem.* **24**, 371 (1952).

³N. A. Lange, *Handbook of Chemistry*, 8th ed., p 1081, Handbook Publishers, Sandusky, 1952.

Figure 48 shows typical data gathered at a fixed stirring speed at 34.55°C. All crystal faces reacted at the same rate when exposed to identical stirring rates at any temperature studied. Figure 49 illustrates the effect of stirring speed on the reaction rates. An increased stirring rate increased the reaction rate at all temperatures observed. The determination of typical rate constants from conductivity data is shown in Fig. 50. When the logarithms of the rate constants determined at the three different stirring speeds were plotted as a function of the reciprocal of the absolute temperature, three straight lines of identical slope were obtained. From these plots the activation energy for the process was determined to be 5800 cal/mole.

The foregoing results indicate that the over-all reaction rate in the system is determined by a diffusion process involving oxygen. All crystallographic faces of copper therefore react at the same rate under the conditions of these experiments.

Surface Effects. — Although faceting and pitting are frequently observed when single crystalline metals undergo aqueous dissolution, the effect of various kinetic conditions on this process is not clear. It is important, therefore, that observations of surface changes as well as kinetic data be

Fig. 48. Per Cent of Unreacted O_2 in Solution (1.2×10^{-2} M Ethylenediamine).

Fig. 49. Effect of Stirring Speed on Reaction Rate.

Fig. 50. Reaction Rate.

recorded if a better understanding of the processes involved is to be gained.

In dilute aqueous ethylenediamine the (110) surface rapidly developed facets which are thought to be (100) faces. At the earliest observable stages only faceting could be seen. No pitting or arrays of pits which could be related to crystal imperfections were detected. Figure 51 illustrates a typically faceted (110) surface resulting from removal of an amount of copper corresponding to an average of 3000 atomic layers. Clearly the surface is no longer (110) but rather a series of facets superimposed on the original (110) base.

In the earlier stages of the reaction the (111) surface did exhibit arrays of pits which could correspond to defect structures in the crystal; however, as the reaction progressed, large facets which obliterated such effects were developed. The facets of (110) orientation shown in Fig. 52 are typical of those which developed during the removal of copper corresponding to an average of 750 atomic layers.

Like the (111) surface, the (100) exhibited structural effects which were thought to be related to crystal defects. Where the former were observed as pits, indicating greater than average reaction at these points, the latter were seen to be hillocks in which the reaction was not so great. Even when an amount of copper corresponding to an

Fig. 51. (110) Copper Surface Showing Development of (100) Facets After Removal of 3000 Atomic Layers in Dilute Ethylenediamine. 8650X.

average of 3000 atomic layers had been removed, no regular faceted structure was observed, as is shown in Fig. 53.

The foregoing surface studies did not indicate a clear relationship, in this particular system, between crystal imperfections and the chemical reactivity of copper. Nucleation of reaction sites appears to be a rather random process. The results are understandable in terms of the theory of Cabrera⁴ regarding the role of imperfections in chemical reactivity. These points are treated more extensively in a paper being prepared for publication.

Fig. 52. (111) Surface with (110) Facets After Removal of 750 Atomic Layers of Copper in Dilute Ethylenediamine. 8650X.

Fig. 53. (100) Surface of Copper After Removal of 3000 Atomic Layers in Dilute Ethylenediamine. 8650X.

ETCH PITS AND DISLOCATIONS IN 99.999% COPPER

An etching solution which develops etch pits at dislocations intersecting the (111) face of 99.999% copper has been reported by Lovell and Wernick.⁵ A modification of this solution (composition: 32 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 160 ml of concentrated HCl, 8 ml of glacial acetic acid, 40 drops of bromine, and 75 ml of H_2O) has been used to investigate the behavior of dislocations in annealed and in irradiated copper. This solution will develop etch pits at clean dislocations which intersect faces within about 3° of (111). It was not established that the correspondence between dislocations and etch pits was one to one, but it was at least approximately so.

Photomicrographs of the same area on a (111) face of a 99.999% copper crystal are given in Fig. 54 and show the as-grown crystal, the crystal as etched after a 10-g-load (1 mil radius point) depression, and after electropolishing and re-etching. New dislocations formed by the point depression were found up to 80μ away from the depression and persisted downward into the crystal. Neutron irradiation of copper at reactor ambient temperature hardens the copper.⁶ A crystal was irradiated with $6 \times 10^{17} \text{ nvt}$, and a 10-g-load point depression was made. The crystal was then etched, and the new dislocations were found to be much closer to the depression, as is shown in Fig. 55.

An irradiated crystal ($6 \times 10^{17} \text{ nvt}$) was subjected to a 500-g-load point depression. The photomicrographs in Fig. 56 show the slip lines after the depression and the new dislocations after etching.

The maximum distance from the point depression for which new dislocations were observed in unirradiated and irradiated copper is given in Table 7.

Since the slip structure was so complicated for the irradiated crystals, it was not possible to use this information to determine the cause of the hardening of copper by irradiation.

⁴N. Cabrera, p 327-48 in *Semiconductor Surface Physics* (R. H. Kingston, ed.), University of Pennsylvania Press, Philadelphia, 1956.

⁵L. C. Lovell and J. H. Wernick, *J. Appl. Phys.* 30, 590 (1959).

⁶T. H. Blewitt (unpublished results).

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Fig. 54. Etch Pits at Dislocations on Annealed Copper. (a) As grown and etched; (b) after 10-g point deformation and etching; (c) after electropolishing and etching. 200X.

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Fig. 55. Etch Pits at Dislocations on Copper Irradiated 6×10^{17} nvt, After 10-g Point Deformation and Etching. 200X.

EVIDENCE FOR DISLOCATION REACTIONS IN COPPER

A 99.999% copper crystal, $3 \times 1 \times 0.1$ cm, of the orientation shown in Fig. 57 was irradiated in the ORNL Graphite Reactor at ambient temperature with 10^{18} nvt. It was then subjected to a bending deformation, and the development of slip lines was observed. The crystal was then etched so as to reveal the dislocations as etch pits. The particular arrangements of the slip lines after the deformation and the location of the dislocations observed on subsequent etching can be accounted for on the basis of the geometry of slip systems in the face-centered cubic system and the interactions of dislocations.

The crystal was bent, by a 4-point bending jig, about the $[\bar{1}01]$ axis to a radius of curvature of approximately 10 cm. Very faint slip lines corresponding to $(\bar{1}11)$ and $(11\bar{1})$ planes were seen in the central portion of the convex (111) surface. No evidence of interaction between these lines was observed. That is, no joggling of the lines on intersection and no increase in the height of the slip line near intersection points were observed.

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Fig. 56. 500-g Point Deformation on Copper Irradiated 6×10^{17} nvt. (a) Slip lines; (b) etch pits at dislocations. 200X.

Table 7. Distance of Dislocation Travel in Irradiated and Unirradiated Copper

Irradiation (nvt)	Travel Distance (μ)	
	10-g Load	100-g Load
Unirradiated	80	140
10^{17}	55	135
4×10^{17}	35-40	130
6×10^{17}	25-30	130

(see Fig. 58). Toward the ends of the crystal, over the points on which the crystal rested in the bending jig, another set of slip lines was observed. These lines corresponded to the $(\bar{1}\bar{1}1)$ plane, and the step height of the lines was very large. The faint lines from the $(\bar{1}\bar{1}1)$ and $(11\bar{1})$ planes crossed these big slip lines and were much more pronounced in the vicinity of such an intersection. An electron micrograph of a carbon replica of such an intersection is shown in Fig. 59.

On etching the crystal with the dislocation etch some new dislocations were seen in the central part of the crystal. Figure 60 shows the etch pits in the same area as the slip lines shown in Fig. 58. It can be seen that there are new dislocations corresponding to a few of the slip lines and particularly at some intersections of the lines.

Rows of pits were found corresponding to the $(\bar{1}\bar{1}1)$ slip lines. Thus, many dislocations were left in the crystal after slip on this plane. Many pits occurred where the $(11\bar{1})$ and $(\bar{1}\bar{1}1)$ lines had crossed the $(\bar{1}\bar{1}1)$ lines, and they corresponded to

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Fig. 57. Orientation of Crystal Before Bending.

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Fig. 58. Slip Lines in Central Portion After 10-cm-Radius Bend. 200X.

the former lines for a short distance away from the $(\bar{1}\bar{1}1)$ lines (Fig. 61).

The above facts can be accounted for on the basis of the geometry of the face-centered cubic slip systems and the interaction of dislocations. The slip planes and slip directions with the

relative resolved shear stress for each system for bending a crystal with this orientation are given in Table 8.

The faint slip lines correspond to the $(\bar{1}\bar{1}1)$ - $[0\bar{1}1]$ and $(11\bar{1})$ - $[\bar{1}\bar{1}0]$ systems, which are the

Table 8. Slip Plane, Slip Direction, and Resolved Shear Stress

Slip Plane	Slip Direction	Relative Resolved Shear Stress
$11\bar{1}$	$\bar{1}\bar{1}0$	0
	$10\bar{1}$	0
	$0\bar{1}1$	0
$\bar{1}\bar{1}1$	$0\bar{1}1$	6
	$\bar{1}\bar{1}0$	2
	101	4
$1\bar{1}\bar{1}$	110	4
	$10\bar{1}$	0
	011	4
$11\bar{1}$	$0\bar{1}1$	2
	101	4
	$\bar{1}\bar{1}0$	6

Fig. 59. Electron Micrograph of Interaction of $(\bar{1}\bar{1}1)$ and $(11\bar{1})$ Slip Lines. 10,000X.

Fig. 60. Etch Pits at Dislocations (Same Area Shown in Fig. 58). 200X.

Fig. 61. Etch Pits at Dislocations Showing Interaction of $(\bar{1}\bar{1}1)$ with $(\bar{1}\bar{1}1)$ and $(11\bar{1})$ Systems. 200X.

avored systems for slip. The Burgers vectors for these systems lie in the (111) plane. Therefore, for a crystal truly oriented as in Fig. 57 and atomically smooth, no slip lines corresponding to these two systems could be seen on the (111) surface. From the electron micrograph of the cutting of a $(\bar{1}\bar{1}1)$ line by a $(1\bar{1}\bar{1})$ line (Fig. 59), it can be seen that the length of the jog in the $(\bar{1}\bar{1}1)$ line is approximately equal to the height of the $(1\bar{1}\bar{1})$ line. Therefore the amount of slip in the $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ planes was actually $\sim 1000 \text{ \AA}$, the lines being faint because the slip vectors lie nearly in the surface being examined. The $(\bar{1}\bar{1}1)$ planes slipped only near the ends of the crystal around the points of contact with the bending jig. The direction and magnitude of the stress on the various planes are not known in these regions, but it is probable that both the $(\bar{1}\bar{1}1)$ - $[110]$ and $(\bar{1}\bar{1}1)$ - $[011]$ systems were operative. Dislocations with Burgers vectors $a/2[110]$ and $a/2[011]$ would repulse each other. Therefore, if the two systems operated on $(\bar{1}\bar{1}1)$, it would be expected that the slip band resulting would change rapidly along the length of the line and that many dislocations would be left along the line. This hypothesis is in agreement with the experimental observations.

The observation of the increase in step height of $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ slip lines on intersection with $(\bar{1}\bar{1}1)$ lines and the subsequent finding of dislocations in the $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ lines near these intersections indicate an interaction between these slip systems. The equations for the possible dislocation reactions on the $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ planes are given below:

$$\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[1\bar{1}0] = \frac{a}{2}[101] \quad (1)$$

$$\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[\bar{1}\bar{1}0] = \frac{a}{2}[\bar{1}\bar{2}1] \quad (2)$$

$$\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[011] = \frac{a}{2}[002] \quad (3)$$

$$\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[0\bar{1}\bar{1}] = \frac{a}{2}[0\bar{2}0] \quad (4)$$

Reaction (1) will occur because the energy is decreased, while reaction (2) indicates a repulsion between the dislocations. For reactions (3) and

(4) no change in energy is involved, but $a/2[002]$ is not a slip vector. The dislocation of Burgers vector $a/2[101]$ which is formed by reaction (1) lies in the $(\bar{1}\bar{1}1)$ plane and thus it can move in that plane. Since $a/2[101]$ has a screw component on intersection with (111) (the surface examined here), when it moves on $(\bar{1}\bar{1}1)$ it leaves a large step. This accounts for the increase in step height of the slip lines corresponding to $(\bar{1}\bar{1}1)$ near the intersections with $(1\bar{1}\bar{1})$. Since the $a/2[101]$ dislocations are held at one end, they can move only a relatively short distance along $(\bar{1}\bar{1}1)$. Thus pits corresponding to these dislocations are seen close by the intersection points of the two slip planes. These dislocations are not pile-ups in the usual sense of this term. From the symmetry of the face-centered cubic system the intersection $(11\bar{1})$ with $(\bar{1}\bar{1}1)$ should act in a similar way. From the dislocation reactions for these planes it is found that the $a/2[011]$ on $(\bar{1}\bar{1}1)$ dislocations react with $a/2[1\bar{1}0]$ on $(1\bar{1}\bar{1})$ in the same way as described above.

The fact that few dislocations are found along the $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ slip lines indicates that the dislocations moved large distances. From Fig. 60 it is obvious that subboundaries in the crystal rarely stopped these dislocations.

From the observation of the intersections of $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ slip lines and from the positions of dislocations after slip as revealed by etch pits, it is clear that these slip systems do not interact in the same way as that described above. The dislocation reactions for these systems are:

$$\frac{a}{2}[0\bar{1}1] + \frac{a}{2}[1\bar{1}0] = \frac{a}{2}[1\bar{2}1] \quad (5)$$

$$\frac{a}{2}[01\bar{1}] + \frac{a}{2}[1\bar{1}0] = \frac{a}{2}[10\bar{1}] \quad (6)$$

Reaction (5) describes a repulsive interaction; (6) is the Lomer reaction. The dislocation $a/2[10\bar{1}]$ formed by this reaction is sessile because the line of the dislocation does not lie in either the (111) or the $(\bar{1}\bar{1}1)$ planes for which $[10\bar{1}]$ is a proper slip vector. (As pointed out by Cottrell, for metals in which the dislocations are extended this reaction would result in a truly sessile dislocation.) The difference between (5) and (6) is merely the sign of one or the other Burgers vector.

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Thus whether or not interaction occurred would be a statistical question. If reaction occurred (6), the only change in the slip lines on intersection would be a diminution of the step height immediately prior to the intersection. (Since these slip lines are faint, such an effect cannot be detected.) The dislocations would then be piled up at the intersection. If, on the other hand, no reaction occurred (5), there would be no observable effect of the intersecting of the slip lines nor any dislocations left near the intersections. This explanation is in qualitative agreement with the

experimental observations, as can be seen in Figs. 58 and 60.

Thus the appearance of the slip lines and the subsequent location of the dislocations are accounted for by dislocation interactions. It should be noted that the effects observed here would be seen only on hardened crystals. For annealed crystals, if dislocation interaction occurred on one plane, the slip process would simply shift to an adjacent plane before an observable number of dislocations had piled up in one place.

DIFFUSION OF DEUTERIUM IN DEUTERON-IRRADIATED COPPER

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A. L. Southern

W. R. Willis¹

The diffusion rates of hydrogen in metals are of general metallurgical and physical interest, as well as being of some importance in certain thermonuclear devices. In the previous report² an experiment was described for measuring the diffusion rate of deuterium in metals by means of an accelerator technique. The method consists of monitoring the neutrons produced from the $D(d,n)He^3$ reaction in a metal target irradiated with D^+ ions from a Cockcroft-Walton accelerator. The analysis developed here differs in several respects from the earlier version² and is far more satisfactory in explaining the experimental results.

Theory

Model of the Diffusion Process. — It is assumed that the target thickness (500 to 5000 μ) is enough greater than the range of the incident deuterons (about 2 μ) that the target may be regarded as infinitely thick. It is also assumed that the deuteron beam is large in diameter (about 1000 μ) compared with the deuteron range and is uniform in current density over its cross section, permitting application of the one-dimensional diffusion equation. In particular, broadening of the beam in the slowing-down process is ignored. The deuteron beam, of initial energy E_0 and current density i , is incident on the planar surface of the target, which is taken as the origin of the penetration coordinate, x . As the beam particles penetrate the target, their mean energy, E , decreases until it reaches zero at the mean deuteron range, $x = R$, producing there a source of diffusing deuterium. The phenomenon of straggling³ causes the source of diffusing particles to have a finite thickness, the distribution in space generally being taken as Gaussian. In order to simplify the analysis, this Gaussian distribution has been replaced by a square wave of width $2\beta R$ and height $i/2\beta R$, centered on the mean range $x = R$. The fractional half width of the source, β , is the quantity termed the "straggle" by nuclear physicists.³

According to this model, the deuterium concentration obeys the differential equation

$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial u^2} + S(u) , \quad (1)$$

where $c(u, \theta)$ is the deuterium concentration, $u = x/R$, $\theta = Dt/R^2$, t is the time, D is the diffusion coefficient, and the source is given by

$$S(u) = \begin{cases} 0 , & 0 \leq u \leq 1 - \beta , \\ \frac{iR}{2\beta D} , & 1 - \beta \leq u \leq 1 + \beta , \\ 0 , & 1 + \beta \leq u \leq \infty . \end{cases} \quad (2)$$

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²M. T. Robinson *et al.*, *Solid State Ann. Prog. Rep. Aug. 31, 1958*, ORNL-2614, p 78-84.

³See, for example, H. Bethe and J. Ashkin, *Experimental Nuclear Physics* (ed. by E. Segrè), vol 1, p 242-48, Wiley, New York, 1953.

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The following initial and boundary conditions have been adopted, in addition to continuity conditions at $u = 1 \pm \beta$:

$$\begin{aligned} c(u, 0) &= 0, \\ c(0, \theta) &= \gamma \left(\frac{\partial c}{\partial u} \right)_{u=0}, \\ \lim_{u \rightarrow \infty} c(u, \theta) &= 0. \end{aligned} \quad (3)$$

The parameter γ is a surface resistance. If the Laplace transform of Eq. (1) with respect to θ is solved, the solution is

$$\bar{c}(u, s) = \frac{iR}{4\beta D s^2} \left[e^{-s^{1/2}(1-\beta)} - e^{-s^{1/2}(1+\beta)} \right] \left[e^{s^{1/2}u} - \frac{1 - \gamma s^{1/2}}{1 + \gamma s^{1/2}} e^{-s^{1/2}u} \right], \quad 0 \leq u \leq 1 - \beta, \quad (4a)$$

$$\bar{c}(u, s) = \frac{iR}{2\beta D s^2} \left\{ 1 - \frac{1}{2} \left[e^{s^{1/2}(1-\beta-u)} + e^{-s^{1/2}(1+\beta-u)} + \frac{1 - \gamma s^{1/2}}{1 + \gamma s^{1/2}} \left(e^{-s^{1/2}(1-\beta+u)} - e^{-s^{1/2}(1+\beta+u)} \right) \right] \right\}, \quad (4b)$$

$1 - \beta \leq u \leq 1 + \beta,$

$$\bar{c}(u, s) = \frac{iR}{4\beta D s^2} \left[e^{s^{1/2}(1+\beta-u)} - e^{s^{1/2}(1-\beta-u)} + \frac{1 - \gamma s^{1/2}}{1 + \gamma s^{1/2}} \left(e^{-s^{1/2}(1+\beta+u)} - e^{-s^{1/2}(1-\beta+u)} \right) \right], \quad (4c)$$

$1 + \beta \leq u \leq \infty,$

where $\bar{c}(u, s)$ is the transform of $c(u, \theta)$ and s is the transform variable. Equations (4) may be readily inverted by the use of standard tables⁴ but, since the inverted solutions are not employed in the sequel, the results will not be given here.

The cross section for the $D(d, n)He^3$ reaction is a strong function of the deuteron energy. It falls so rapidly as an incident deuteron penetrates a solid target that, as long as β is reasonably small, the entire solution to the diffusion equation may be adequately represented by the expansion of Eq. (4a) about $u = 0$. If the exponentials in the right-hand factor of (4a) are expanded, the result is

$$\bar{c}(u, s) = \frac{iR}{2\beta D} \cdot \frac{e^{-s^{1/2}(1-\beta)} - e^{-s^{1/2}(1+\beta)}}{s^{3/2}(1 + \gamma s^{1/2})} \sum_{n=0}^{\infty} s^n \left[\frac{\gamma u^{2n}}{(2n)!} + \frac{u^{2n+1}}{(2n+1)!} \right]. \quad (5)$$

Defining the functions

$$\bar{C}_n(s) = \frac{s^{n-3/2}}{1 + \gamma s^{1/2}} \left[e^{-s^{1/2}(1-\beta)} - e^{-s^{1/2}(1+\beta)} \right], \quad (6)$$

⁴A. Erdelyi (ed.), *Tables of Integral Transforms*, vol 1, p 246-47, McGraw-Hill, New York, 1954.

Eq. (5) may be written as

$$\bar{c}(u, s) = \frac{iR}{2\beta D} \sum_{n=0}^{\infty} \left[\frac{\gamma u^{2n}}{(2n)!} + \frac{u^{2n+1}}{(2n+1)!} \right] \bar{C}_n(s) ,$$

and the solution to Eq. (1) is then

$$c(u, \theta) = \frac{iR}{2\beta D} \sum_{n=0}^{\infty} \left[\frac{\gamma u^{2n}}{(2n)!} + \frac{u^{2n+1}}{(2n+1)!} \right] C_n(\theta) , \quad 0 \leq u \leq 1 - \beta . \quad (7)$$

The $C_n(\theta)$ may be found by using standard tables⁴ to invert the $\bar{C}_n(s)$. The first three of these are:

$$C_0(\theta) = (1 + \beta + \gamma) \operatorname{erfc} \frac{1 + \beta}{2\theta^{1/2}} - (1 - \beta + \gamma) \operatorname{erfc} \frac{1 - \beta}{2\theta^{1/2}} + \theta^{1/2} \left(\operatorname{erf}' \frac{1 - \beta}{2\theta^{1/2}} - \operatorname{erf}' \frac{1 + \beta}{2\theta^{1/2}} + \gamma^2 C_1(\theta) \right) , \quad (8a)$$

$$C_1(\theta) = \frac{1}{\gamma} e^{\theta/\gamma^2} \left[e^{(1-\beta)/\gamma} \operatorname{erfc} \left(\frac{1 - \beta}{2\theta^{1/2}} + \frac{\theta^{1/2}}{\gamma} \right) - e^{(1+\beta)/\gamma} \operatorname{erfc} \left(\frac{1 + \beta}{2\theta^{1/2}} + \frac{\theta^{1/2}}{\gamma} \right) \right] , \quad (8b)$$

$$C_2(\theta) = \frac{C_1(\theta)}{\gamma^2} + \frac{1}{2\theta\gamma} \left\{ \frac{\theta^{1/2}}{\gamma} \left(\operatorname{erf}' \frac{1 + \beta}{2\theta^{1/2}} - \operatorname{erf}' \frac{1 - \beta}{2\theta^{1/2}} \right) + \frac{1}{2\theta^{1/2}} \left[(1 - \beta) \operatorname{erf}' \frac{1 - \beta}{2\theta^{1/2}} - (1 + \beta) \operatorname{erf}' \frac{1 + \beta}{2\theta^{1/2}} \right] \right\} , \quad (8c)$$

where the error functions are defined by

$$\operatorname{erfc} x = 1 - \operatorname{erf} x = 2\pi^{-1/2} \int_x^{\infty} e^{-u^2} du ,$$

$$\operatorname{erf}' x = \frac{d}{dx} \operatorname{erf} x = 2\pi^{-1/2} e^{-x^2} .$$

The $D(d,n)\text{He}^3$ Cross Section. — In order to fit Eq. (7) to experimental data, it is necessary to develop an expression for the $D(d,n)\text{He}^3$ cross section as a function of penetration. Since this cross section follows the Gamow relation quite accurately,⁵ it may be written as

$$\sigma(\epsilon) = \epsilon^{-1} \exp \left(-\frac{A}{E_0^{1/2}} \cdot \frac{1 - \epsilon^{1/2}}{\epsilon^{1/2}} \right) , \quad (9)$$

where $\epsilon = E/E_0$ is the relative deuteron energy, A is the Gamow slope, and the cross section is normalized to $\sigma(1) = 1$.

From experimental data on energy loss rates ($-dE/dx$), ϵ can be determined as a function of penetration, and hence a function $\sigma(u)$ can be derived. Unfortunately, data on the slowing down of protons

⁵G. A. Sawyer and J. A. Phillips, *Survey of Several of the Reactions Occurring When Lithium and Beryllium Are Bombarded by Protons and Deuterons of 30–250 kev*, LA-1578 (August 1953).

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and deuterons in metals⁶ do not extend to sufficiently low energies for this procedure to be applied over the entire energy range. Below the limit of the empirical data, the Fermi-Teller equation⁷ has been employed:

$$\frac{-dE}{dx} = BE^{1/2} \quad (10)$$

Integration of this expression yields

$$\epsilon = \begin{cases} (1-u)^2, & 0 \leq u \leq 1, \\ 0, & 1 \leq u \leq \infty, \end{cases} \quad (11)$$

if it is assumed that (10) applies over the entire energy range (as it certainly does not). From Eqs. (9) and (11),

$$\sigma(u) = \begin{cases} (1-u)^{-2} e^{-ku/(1-u)}, & 0 \leq u \leq 1, \\ 0, & 1 \leq u \leq \infty. \end{cases} \quad (12)$$

Equation (12) cannot be expected to be especially accurate due to the inadequacy of (10), but if the parameter k is empirically adjusted instead of being set to $AE_0^{-1/2}$, surprisingly good agreement can be obtained between values of $\sigma(u)$ based on Eq. (12) and values computed by using experimental $(-dE/dx)$ data to evaluate $\sigma(u)$. Table 9 illustrates this agreement for 176-keV deuterons incident on copper.

⁶S. K. Allison and S. D. Warshaw, *Revs. Modern Phys.* 25, 779-817 (1954).

⁷M. Gryzinski, *Phys. Rev.* 107, 1471-75 (1957).

Table 9. D(d,n)He³ Cross Section vs Penetration into Copper

Range (calc) = 1.63 μ

$AE_0^{-1/2} = 3.347$

k [Eq. (12)] = 3.2662

u	E (keV)	$\sigma(u)$		u	E (keV)	$\sigma(u)$	
		"Empirical"	Eq. (12)			"Empirical"	Eq. (12)
0.00	176	1.000	1.000	0.50	45	0.147	0.153
0.05	160	0.934	0.933	0.55	37	0.088	0.091
0.10	145	0.863	0.860	0.60	29	0.043	0.047
0.15	130	0.783	0.778	0.65	22	0.017	0.019
0.20	115	0.691	0.691	0.70	16	0.007	0.005
0.25	100	0.590	0.598	0.75	11	0.001	0.001
0.30	88	0.500	0.503	0.80	7	0.000	0.000
0.35	76	0.403	0.408	0.85	4	0.000	0.000
0.40	65	0.313	0.315	0.90	2	0.000	0.000
0.45	55	0.228	0.228	0.95	1	0.000	0.000
0.50	45	0.147	0.153	1.00	0	0.000	0.000

The "empirical" values of $\sigma(u)$ were obtained by graphical integration of $-dE/dx$ vs E for $E \geq 100$ kev, using the "best" values recommended by Allison and Warshaw⁶ for the slowing down of protons in copper, coupled with the use of Eq. (10) for $E < 100$ kev. The integration produced values of the deuteron range, R , and of $\epsilon(u)$, from which the table was constructed using the cross-section data of Sawyer and Phillips.⁵ Similarly gratifying agreement has been obtained both for the $D(d,n)He^3$ reaction and for the $Be^9(d,n)B^{10}$ reaction,⁸ with 176-kev deuterons incident on beryllium.

It is convenient to define the integrals

$$B_n(k) = \frac{k}{n!} \int_0^\infty u^n \sigma(u) du \quad (13)$$

Inserting Eq. (12) into (13), performing one integration by parts, and substituting $v = k/(1-u)$ yields

$$B_n(k) = \frac{e^k}{n!} \int_k^\infty \left(1 - \frac{k}{v}\right)^n e^{-v} dv \quad (14)$$

Straightforward integration produces

$$\begin{aligned} B_0(k) &= 1, \\ B_1(k) &= 1 - ke^k E_1(k), \\ &\vdots \\ B_n(k) &= \frac{[2(n-1) + k] B_{n-1}(k) - B_{n-2}(k)}{n(n-1)}, \end{aligned} \quad (15)$$

where $E_1(k)$ is the exponential integral function

$$E_1(k) = \int_k^\infty v^{-1} e^{-v} dv.$$

Values of the $B_n(k)$ are readily computed, either from tables⁹ or, more conveniently for machine computations, from an approximation to $E_1(k)$ given by Hastings.¹⁰ Table 10 presents the first few $B_n(k)$ for 176-kev deuterons incident on copper. Their rapid decrease with increasing n reflects the rapid decrease in the $D(d,n)He^3$ cross section with increasing penetration.

Neutron Counting Rate Function. — The rate of production of neutrons from $D(d,n)He^3$ reactions in a target which are detected by a counter may be written as

$$P(t) = iR\sigma_0 AF \int_0^\infty \sigma(u) c(u, \theta) du \quad (16)$$

where σ_0 is the $D(d,n)He^3$ cross section at the incident deuteron energy, A is the cross-sectional area

⁸D. C. Ralph and F. E. Dunham, *Phys. Rev.* **98**, 249 (1954).

⁹*Tables of the Sine, Cosine, and Exponential Integrals*, Federal Works Administration, Works Projects Administration, New York, 1940.

¹⁰C. Hastings, Jr., *Approximations for Digital Computers*, p 190, Princeton University Press, Princeton, 1955.

Table 10. The Cross-Section Integrals $B_n(k)$

$$k = 3.2662$$

n	$B_n(k)$	n	$B_n(k)$
0	1.0000 0000	5	0.0000 3808
1	0.2016 4399	6	0.0000 0313
2	0.0309 4879	7	0.0000 0023
3	0.0038 7268	8	0.0000 0002
4	0.0004 1135	9	0.0000 0000

of the beam, and F is a neutron detector geometry and efficiency factor. By defining the parameter

$$\alpha = \frac{i^2 R^2 \sigma_0 A F}{Dk} \quad (17)$$

and introducing Eqs. (7) and (13) into (16), the following result is obtained:

$$P(t) = \alpha \sum_{n=0}^{\infty} \frac{\gamma B_{2n}(k) + B_{2n+1}(k)}{2\beta} C_n(\theta) \quad (18)$$

Equation (18) is used to fit experimental data by the method of least squares. The four parameters α , β , γ , and $\delta = D/R^2$ are available for adjustment. The cross-section parameter, k , is chosen as described above for each deuteron energy-target metal combination.

A numerical study was made of the successive terms of Eq. (18) with the IBM-704 digital computer at ORGDP. A wide range of values of θ was used with each of several combinations of β and γ . In every case, convergence compatible with experimental counting rate errors was obtained with four terms of the series.

It is of some interest to examine the asymptotic form of Eq. (18) for long times. For $\theta \gg 1 \pm \beta$, the arguments $(1 \pm \beta)/2\theta^{1/2}$ of the error functions in Eqs. (8a) and (8c) become small enough to use the well-known convergent expansions of the exponential and of $\operatorname{erf} x$ (ref 11) truncated at a few terms. The arguments

$$\frac{1 \pm \beta}{2\theta^{1/2}} + \frac{\theta^{1/2}}{\gamma}$$

of the error functions in Eq. (8b) have minima for $\theta_{\min} = \gamma(1 \pm \beta)/2$, the arguments being $[2(1 \pm \beta)/\gamma]^{1/2}$. For $\theta \gg \theta_{\min}$ or, if γ is small enough, in any case, the asymptotic expansion of $\operatorname{erfc} x$ (ref 11) may be employed. The result of using these expansions, to terms in $t^{-3/2}$, is

$$P(t) = a - bt^{-1/2} + ct^{-3/2} - O(t^{-5/2}), \quad t \rightarrow \infty, \quad (19)$$

¹¹A. Erdelyi (ed.), *Higher Transcendental Functions*, vol 2, p 147; McGraw-Hill, New York, 1953.

where

$$a = \alpha[\gamma B_0(k) + B_1(k)] , \quad (20a)$$

$$b = \frac{a(1+\gamma)}{\pi^{1/2} \delta^{1/2}} , \quad (20b)$$

$$c = \frac{a}{12\pi^{1/2} \delta^{3/2}} \left\{ (1+\gamma) \left[3 + \beta^2 + 6 \frac{\gamma B_2(k) + B_3(k)}{\gamma B_0(k) + B_1(k)} + 6\gamma^2 \right] - 2 - \frac{6}{\gamma^2} \cdot \frac{\gamma B_4(k) + B_5(k)}{\gamma B_0(k) + B_1(k)} \right\} . \quad (20c)$$

The usefulness of Eq. (19) is severely limited for estimation of the parameters α , β , γ , and δ , primarily because the asymptotic expansion of $\operatorname{erfc} x$ is not accurate enough. Nevertheless, every set of experimental data which has been examined obeys the general form of (19) very accurately at long times. The value of the parameter c , however, as given by Eq. (20c), is incorrect, although a and b seem to be satisfactory.

If the deuteron straggle is sufficiently small, it is convenient to set $\beta = 0$ and to modify the solutions (4) appropriately. Taking the limit of Eq. (4a) as β approaches zero,

$$\bar{c}(u, s) = \frac{iR}{2Ds^{3/2}} e^{-s^{1/2}} \left(e^{s^{1/2}u} - \frac{1 - \gamma s^{1/2}}{1 + \gamma s^{1/2}} e^{-s^{1/2}u} \right) , \quad 0 \leq u \leq 1 . \quad (4a')$$

The coefficients of the transform series, Eq. (6), may now be defined by

$$\bar{C}_n(s) = \frac{s^{n-1}}{1 + \gamma s^{1/2}} e^{-s^{1/2}} , \quad (6')$$

and the solution to the differential equation becomes

$$c(u, \theta) = \frac{iR}{D} \sum_{n=0}^{\infty} \left[\frac{\gamma u^{2n}}{(2n)!} + \frac{u^{2n+1}}{(2n+1)!} \right] C_n(\theta) , \quad 0 \leq u \leq 1 . \quad (7')$$

The first three $C_n(\theta)$ are

$$C_0(\theta) = \operatorname{erfc} \frac{1}{2\theta^{1/2}} - e^{1/\gamma + \theta/\gamma^2} \operatorname{erfc} \left(\frac{1}{2\theta^{1/2}} + \frac{\theta^{1/2}}{\gamma} \right) , \quad (8a')$$

$$C_1(\theta) = \frac{1}{2\gamma\theta^{1/2}} \operatorname{erf}' \frac{1}{2\theta^{1/2}} - \frac{1}{\gamma^2} e^{1/\gamma + \theta/\gamma^2} \operatorname{erfc} \left(\frac{1}{2\theta^{1/2}} + \frac{\theta^{1/2}}{\gamma} \right) , \quad (8b')$$

$$C_2(\theta) = \frac{1}{\gamma^2} C_1(\theta) + \frac{1}{4\gamma\theta^{3/2}} \left[\frac{1}{2\theta} - 1 + \frac{1}{\gamma} \right] \operatorname{erf}' \frac{1}{2\theta^{1/2}} . \quad (8c')$$

Finally, the neutron counting rate equation becomes

$$P(t) = \alpha \sum_{n=0}^{\infty} [\gamma B_{2n}(k) + B_{2n+1}(k)] C_n(\theta) \quad (18')$$

and only three parameters, α , γ , and δ , remain to be adjusted. The inverse power series (19) is unchanged as long as β is set to zero in Eq. (20c).

Data Processing System. — A set of experimental data consists of a list of numbers proportional to the neutron counting rate, obtained at equal intervals of time, from which it is desired to deduce values of the four parameters α , β , γ , and δ . The necessary operations are carried out by two digital computer programs.

Input to the first program, performed on the Oracle, consists of a punched paper tape containing the observations. The paper tapes have, until recently, been prepared manually from an adding machine printed tape original. They are now prepared directly from the output of the scaler by means of a special paper tape punch designed and built in the Instrumentation and Controls Division. In the Oracle program the observations are converted to counting rates, corrected for background and for neutron detector dead-time losses, and then written on magnetic tape to form a permanent file record of the data. The method of least squares is then used to fit Eq. (19) to all but the first 128 points (usually) of the data set. The data are now examined for points with residuals more than nine times the minimized sum of residuals of the complete set of data (the 99.73% confidence level). If such points are detected, another least-squares fit of Eq. (19) is made, omitting the "bad" points. The entire procedure is repeated until the same number of points is rejected on two successive cycles. As an example, the data from target 36 consisted of 1354 observations. Of these, the last 1226 were used in the fit of Eq. (19). The program located 27 points falling beyond the 99.73% confidence limits (about $\pm 3\%$ in this case) and employed the remaining 1199 points in the final cycle of least squares. The next step in the program is to use Eqs. (20), assuming $\beta = 0$, to estimate values of α , γ , and δ . These results, the parameters of Eq. (19), a list of the rejected points, and certain statistical measures comprise the first section of output of the program. The program then produces a special output tape (punched paper), which is used in making plots of the observations. Finally, another output tape is produced for use as input to the second computer program. The entire procedure described here requires about 10 min for a data set of about 1300 points.

One of the output tapes from the Oracle program is used to program an x-y recorder to plot the observations automatically on 11×17 in. graph paper. The original of Fig. 62 was produced in this way. The other output paper tape is transcribed onto punched cards by an IBM-46 paper tape to card punch. The resulting card deck, eight observations per card, is copied onto IBM magnetic tape for use as input to a program carried out on an IBM-704 computer.

The original intention of obtaining reasonable initial estimates of the parameters by fitting Eq. (19) to the data has been frustrated by the inadequacy of the asymptotic expansion of $\operatorname{erfc} x$. This results from the rather large values of γ that are required to fit the data. Nevertheless, it has proved useful to employ Eq. (19) for smoothing the data, in the sense of detecting those observations which are likely to be erroneous due (primarily) to malfunctioning of the counting equipment.

The second computer program, performed on the IBM-704 machine at ORGDP, fits Eq. (18) to the data by the method of least squares. Input to this program consists of the data, as corrected by the

Fig. 62. Counting rate of $D(d,n)He^3$ Neutrons Produced in Copper at $18^\circ C$ by 176-kev Deuterons.

Oracle, written on magnetic tape, of initial estimates of α , β , γ , and δ , and of certain control information written on punched cards. The program automatically repeats least-squares cycles until convergence is obtained. Unfortunately, since the problem is nonlinear, it is not possible (in general) to vary all four parameters simultaneously without running into trouble. Hence the program allows the variation of any desired combination of the parameters, the remaining ones being held fixed. After each least-squares cycle is completed, the new parameters, their standard deviations, and certain statistical information are written on magnetic tape for later examination. After convergence is attained, the calculated counting rates and their standard deviations are written also.

The general procedure in using this routine is to refine α and δ together, holding γ and β constant, until convergence is reached. Then α , γ , and δ are refined. It has not proved possible to vary β by least squares (see below). Each least-squares cycle requires approximately 3 min of machine time for 1300 observations. Normally, about six cycles are required to complete the analysis, divided into two or three sessions on the machine.

The selection of appropriate weights for the observations is difficult. Since the observations themselves are numbers of counts, they are, presumably, samples of Poisson-distributed populations. This would suggest using $w(P)$ proportional to P^{-1} . On the other hand, the approximations inherent in the mathematical development given above become less important for longer times, that is, for larger values

of P . This is true both of the series expansion of $c(u, \theta)$, Eq. (7), and of the cross-section approximation, Eq. (12). Furthermore, experimental difficulties, particularly with long-term stability of the deuteron beam current, both spatial and temporal, make the scatter of the observations much greater than would be expected from counting statistics alone. For example, in the latter part of the data on target 36, the number of counts recorded in each observation was about 4×10^5 . The expected statistical variation is ± 630 counts or $\pm 0.16\%$. The actual variation is more nearly $\pm 10^4$ counts or $\pm 2.5\%$. All of this suggests that unit weights may be more appropriate than the Poisson weights.

Agreement between observed and calculated data sets is expressed in terms of the agreement index

$$R = \left[\frac{\sum w(P_{\text{obs}} - P_{\text{calc}})^2}{\sum wP_{\text{obs}}^2} \right]^{1/2} \quad (21)$$

modeled on the one used in x-ray crystallography. The summations extend over all observations. Values of R near 1 or 2% are considered to be measures of excellent agreement of the data with Eq. (18). Figure 62 shows also the error band, computed from the variance-covariance matrix produced from the least-squares procedure. The bands shown are standard deviations (68.27% confidence level).

Experimental

The experimental procedure is substantially the same as that described in the previous report.² The principal changes in the neutron-detecting equipment are the use of a Berkeley model 7360 timer-scaler in place of the more limited model 7350 used before and the replacement of the Berkeley model 1452 digital recorder with a paper tape punching unit. Target temperature control is now achieved by spraying the back of the target with ethanol which is circulated in a closed system. The ethanol is chilled by a dry ice-ethanol slush and then heated to the desired temperature by a small electric tube furnace. Temperature control is achieved by a Brown Air-O-Line controller actuated by one of the target thermocouples. This arrangement allows the target temperature to be maintained to within $\pm 1^\circ\text{C}$ in the range from about -50°C to $+50^\circ\text{C}$.

The discovery that there is appreciable resistance to the escape of deuterium from the surface of a copper target has led to the development of an auxiliary ion gun so arranged that targets may be cleaned after mounting in the accelerator vacuum system by bombardment with $\sim 1\text{-keV}$ Ar^+ ions before starting the D^+ irradiations. This gun consists of a Moak-Reese-Good r-f ion source of conventional design followed by a single electrostatic focusing lens. Installation of this equipment for test is planned for the near future.

Experimental Results

The model described above has developed to the present stage during attempts to fit data from the first few successful irradiations with theoretical curves. It was apparent from the beginning that the solution given to the diffusion equation by Fiebiger¹² was entirely inadequate, since it predicts far too

¹²K. Fiebiger, *Z. angew. Phys.* 9, 213-23 (1957).

rapid attainment of a steady-state neutron counting rate. A very major improvement resulted from use of the semiinfinite slab model, even for $\beta = \gamma = 0$. Initial studies of this model, employing a numerical integration of Eq. (16) rather than the series expansion (18), eventually showed that $\gamma = 0$ was not a good choice. This fact eluded us for some time since, if a least-squares refinement is made commencing with $\gamma = 0$, the new γ will invariably be negative, a physical absurdity. On the other hand, if γ is started at some large value, it refines promptly to a positive value. This situation is of very common occurrence in nonlinear least-squares problems. Table 11 shows the effect of including the surface resistance in the diffusion model on agreement of calculated and observed neutron counting rate curves for two copper targets. The marked improvement in R for both targets will be noted.

The effect of including the deuteron straggle, β , is less dramatic. Table 12 shows some results obtained on target 36. Increasing β above 0.05 causes a small but noticeable worsening of the agreement.¹³ Attempts were made to refine β for target 36 by least squares, starting from 0.05, both alone

¹³Direct comparison of Tables 11 and 12 cannot be made, since the computations for the former used data which were not corrected for counter dead-time losses. The changes between the two tables result primarily from the effect of this correction, not from the inclusion of β in the model.

Table 11. Effect of Surface Resistance on Agreement

Target	γ	$\delta(\text{sec}^{-1})$	$\frac{1+\gamma}{\delta^{1/2}}$	R (%)
$\times 10^{-2}$				
34	0	0.355 ± 0.005	16.8	2.48
	1.40 ± 0.05	1.39 ± 0.04	20.4	1.38
36	0	0.134 ± 0.003	27.3	5.73
	6.47 ± 0.28	2.80 ± 0.17	44.6	3.32

Table 12. Effect of Deuteron Straggle on Agreement

(Target 36)

β	γ	$\delta(\text{sec}^{-1})$	$\frac{1+\gamma}{\delta^{1/2}}$	R (%)
$\times 10^{-2}$				
0.05	7.59 ± 0.31	2.60 ± 0.15	53.3	3.175
0.10	7.57 ± 0.31	2.59 ± 0.15	53.2	3.177
0.20	7.53 ± 0.31	2.56 ± 0.15	53.3	3.186
0.30	7.44 ± 0.32	2.52 ± 0.15	53.1	3.200
0.40	7.47 ± 0.32	2.53 ± 0.15	53.2	3.222
0.50	7.43 ± 0.32	2.50 ± 0.15	53.3	3.250

and in combination with the other parameters. In each case a large negative value was obtained. These results suggest that β is quite small; small enough, in fact, that it can reasonably be set to zero.

The asymptotic expansion, Eq. (19), has been found to represent the experimental data very well for long times. However, as noted before, only the first two parameters of this expansion are of any real interest. In Table 13 are given some values of $(1 + \gamma)\delta^{-1/2}$ as determined from the parameters a and b of Eq. (19) for several targets. These values may be compared with those obtained by fitting the complete Eqs. (16) or (18), which are given in Tables 11 and 12. It will be observed that excellent agreement exists for target 36 between the value in Table 12 and that in Table 13. The values in Table 11 for targets 34 and 36 are in fair agreement with those in Table 13, for the $\gamma \neq 0$ case.

Examination of Table 13 shows no correlation of the values of $(1 + \gamma)\delta^{-1/2}$ with target crystallite size or with deuteron beam current. The variation of this quantity over a range of about 4:1 is, therefore, to be attributed to variations of the surface resistance, γ , from target to target.

Attempts to change the weights of the observations from the Poisson values to unit values have been unsuccessful so far, due to problems of interaction among the parameters during the least-squares procedure. In view of the desirability of replacing Eq. (18) with (18'), its equivalent for $\beta \equiv 0$, these attempts have been suspended until a new machine code is completed.

Experiments at other temperatures than 18°C have not yet been analyzed. Qualitatively, there appears to be a temperature effect of the expected sign. The magnitude appears to be rather small, but in view of complications arising from the nonzero surface resistance, this may not actually be true.

Figure 62 shows the experimental data for target 36 and the calculated curve [Eq. (18)] derived for it.

Table 13. Values of $(1 + \gamma)\delta^{-1/2}$ from Asymptotic Equation
(All experiments at $18 \pm 2^\circ\text{C}$)

Target	$(1 + \gamma)\delta^{-1/2}$ (sec ^{1/2})	Deuteron Current (μa)
34 ^a	25.4	84
36 ^b	52.2	80
41 ^b	80.2	80
47 ^b	47.7	137
49 ^c	29.5	94
51 ^{b,d}	91.2, 110	54
55 ^{b,e}	36.0, 56.5	49

^aMachined block; finely crystalline.

^bRolled sheet, coarsely crystalline.

^cSingle crystal.

^dFirst value: last 403 points; second value: last 147 points; total: 531.

^eFirst value: last 690 points; second value: last 433 points; total: 946.

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ALLOY STUDIES

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INTRODUCTION

In a broad sense, this work is concerned with the effect of radiation on transformations in alloys. It is useful to divide these transformations into two types, those that involve a change in composition in the local region of the transformation product (diffusion-controlled reactions) and those that occur by means of a nondiffusive, shear-type displacement (martensitic reactions). Included among the diffusion-controlled transformations are the changes in crystal structure that take place during precipitation from solid solution and the changes in atomic arrangement that are the result of an order-disorder transition. The diffusion-controlled and the martensitic reactions have in common the property that the reaction is *nucleated* at regions of the crystal favorably disposed toward the reaction in question. Since irradiation by high-energy particles or photons introduces regions of high energy which may serve as nucleation sites, it is reasonable to expect transformation reactions to be accelerated in irradiated metals. A second possibility exists for the diffusion-controlled reactions in substitutional alloys where diffusion occurs by a vacancy mechanism. Irradiation-produced vacancies may enhance diffusion, and therefore atomic rearrangements may take place more quickly than in the unirradiated alloy.

These ideas concerning the effect of irradiation in alloys are being tested with experiments on a number of alloys that exhibit various types of transformations.

IRRADIATION EFFECTS ON Cu-Al ALLOYS

Introduction

It has been shown previously^{2,3} that a decrease in the resistivity of alpha-phase Cu-Al alloys takes place upon neutron irradiation at about 40°C. The magnitude of the decrease in resistivity increases with the aluminum content of the alloy,

and no decrease is observed for pure copper. For the 15 at. % Al alloy the decrease in resistivity at 40°C amounts to 0.18 $\mu\text{ohm-cm}$, or about 2%. However, no decrease in resistivity takes place during irradiation at -120°C, although the decrease sets in upon subsequent raising of the temperature above -50°C.

These observations are interpreted to indicate that the alloy is initially in a metastable state and that this metastability is eliminated upon irradiation at 40°C. This is illustrated schematically in Fig. 63. If it were possible to maintain equilibrium during cooling, the resistivity would follow the solid curve, in which the departure from linearity at $T > T_1$ is due to an equilibrium atomic rearrangement such as short-range disordering, local segregation, or formation of point defects. The notion that we wish to employ is that it is virtually impossible to cool the alloy slowly enough to avoid retaining the state of affairs characteristic of a higher temperature T_2 . Thus, under actual conditions the resistivity during cooling is considered to follow the equilibrium curve only until the temperature T_2 is reached. Upon further cooling, the actual resistivity lies above the equilibrium value by an

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Fig. 63. Schematic Illustration of the Retention During Cooling of a Nonequilibrium State Characterized by the Excess Resistivity BC or $B'C'$.

¹Co-op student from Virginia Polytechnic Institute.

²M. S. Wechsler and R. H. Kernohan, *Phys. and Chem. Solids* 7, 307 (1958).

³M. S. Wechsler and R. H. Kernohan, *Solid State Ann. Prog. Rep. Aug. 31, 1958*, ORNL-2614, p 85.

amount corresponding to BC or $B'C'$. However, upon irradiation at 40°C (T_0 in Fig. 63) the metastability is relieved and the resistivity decreases from B' to C' .

As has been described previously,^{3,4} at-temperature measurements of ρ vs T for unirradiated Cu-Al (15 at. % Al) indicate an excess resistivity at temperatures above 200°C . Thus, the temperature T_2 in Fig. 63 may be identified as 200°C . Furthermore, if the decrease of $0.18\ \mu\text{ohm-cm}$ observed upon irradiation is associated with the quantity $B'C'$ or BC , it is possible to evaluate the equilibrium excess resistivity AC . The logarithm of AC was found to vary linearly with $1/T$, corresponding to a formation energy of $0.15\ \text{eV}$.

In-Pile Measurements at Elevated Temperatures

An aspect of the point of view illustrated in Fig. 63 that is subject to experimental test is the effect of varying the irradiation temperature. It can be seen from the figure that, since the alloy is at equilibrium at $T_2 \approx 200^\circ\text{C}$ and above, irradiation at these temperatures should produce no decrease in resistivity. But, when the irradiation temperature is decreased below T_2 , a decrease in resistivity should take place, whose magnitude increases with lower irradiation temperatures corresponding to the distance between the "observed" and "equilibrium" curves in Fig. 63. However, if the irradiation temperature is reduced below, say, -50°C , atomic mobilities will be too low to permit a change in properties even in the radiation environment.

The results of irradiation at temperatures between 45 and 250°C are shown in Fig. 64 for single-crystal samples of Cu-Al (15 at. % Al). It is seen that irradiation at 200 and 250°C produces little change in the resistivity. However, when the irradiation temperature is decreased below 200°C , a decrease in resistivity takes place, whose magnitude increases with decreasing temperature of irradiation. The decrease in resistivity observed at 150°C is approximately one-half of the decrease at 100°C .

The effect of varying the irradiation temperature was also investigated in the "step-irradiation" experiment, illustrated schematically in Fig. 65. In this experiment the sample is irradiated at

successively lower temperatures. In Fig. 65 the normal temperature coefficient of resistivity is indicated by the slope of line LM . Previous measurements have shown² that the irradiation does not affect the temperature coefficient. Upon each change in irradiation temperature, the resistivity is decreased initially due to the change in temperature itself (short-dashed lines parallel to LM). Then, as a result of the irradiation, the diffusion-controlled reaction causes the resistivity

Fig. 64. In-Pile Measurements of Resistivity upon Irradiation at Various Temperatures for Cu-Al (15 at. % Al) Single Crystals. The open and filled triangles refer to separate runs at 150°C .

Fig. 65. Step-Irradiation Experiment (Schematic).

⁴M. S. Wechsler and R. H. Kernohan, *Acta Met.* 7, 599 (1959).

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to decrease further to the equilibrium curve (vertical arrows). Figure 65 indicates that an additional decrease should take place at each irradiation step, although the amount of the decrease should become progressively smaller as the temperature is lowered. Actual measurements, Fig. 66, show that this is the case. The $\Delta\rho$ values in Fig. 66 are with respect to the line JK in Fig. 65 (see brace labeled " $\Delta\rho$ "), and therefore changes arising from the temperature coefficient are canceled out. Thus, the decreases shown in Fig. 66 are a measure of the atomic rearrangements undergone during irradiation, corresponding to the vertical arrows in Fig. 65.

A point that is of some interest concerning the curves shown in Fig. 64 is the kinetics of the decrease in resistivity. When these curves are normalized, the curves of Fig. 67 result, where the ordinate, f , is the fractional departure from the completion of the annealing process defined by the quantity

$$f = \frac{\rho - \rho_f}{\rho_i - \rho_f},$$

where ρ , ρ_i , ρ_f are the resistivities at time t , at the beginning, and at the end of the annealing, respectively. The time, τ , for various fractional amounts of annealing is plotted vs reciprocal

irradiation temperature in Fig. 68. It is seen that τ is given roughly by an equation of the form

$$\tau = \tau_0 \exp \frac{\epsilon_M}{kT},$$

where ϵ_M is the activation energy for motion of the process. In Fig. 69 ϵ_M for these in-pile measurements is plotted vs f and compared with corresponding results for the case where the decrease in resistivity is obtained² subsequent to three weeks' irradiation at -120°C . It is interesting that in the presence of the neutron flux the reaction goes on with an activation energy that is approximately constant, whereas the activation energy increases progressively as

Fig. 67. Normalized In-Pile Decay Curves. Cu-Al (15 at. % Al).

Fig. 66. Step-Irradiation Experiment. In-pile measurements on Cu-Al (15 at. % Al) at successively lower temperatures.

Fig. 68. Times for Various Fractional Amounts of Decrease in Resistivity vs Reciprocal Irradiation Temperature.

the reaction proceeds when the full radiation dose is received at a low temperature prior to bringing the sample to the reaction temperature.

Another comparison to be made between the results of the two types of experiments concerns the shapes of the decay curves. It is possible to construct decay curves characteristic of a given temperature by extrapolating the curves in Fig. 68 for the in-pile decrease in resistivity and, similarly, the curves for the decrease following irradiation at -120°C given in Fig. 10 of ref 2. The results for a reaction temperature of 40°C are shown in Fig. 70. The best fit to the curves was attempted for first-order kinetics (simple exponential decay) with an equation of the form

$$f = \exp\left(-\frac{t-t'}{\tau}\right) \quad (1)$$

Fig. 69. Activation Energy for Annealing vs f . Results are shown for at-temperature in-pile annealing (this report) and for the annealing observed after irradiation at -120°C (Fig. 11, ref 2). The arrows indicate the direction of the reaction.

Fig. 70. Comparison of the Kinetics of In-Pile Annealing at 40°C with Out-of-Pile Annealing at 40°C Following Three Weeks' Irradiation at -120°C . Cu-Al (15 at. % Al).

and for second-order kinetics with an equation of the form

$$f = \frac{1}{1 + (t - t')/\tau} \quad (2)$$

It appears that the in-pile annealing curve can be fitted rather well with Eq. (2), where the relaxation time, τ , is 1120 min and the incubation time, t' , is 155 min. However, neither equation is capable of describing the decrease in resistivity after irradiation at -120°C , since the observed decrease is too rapid at short times and too slow at long times. This is a consequence of the low initial activation energy for the annealing and the rapid increase in activation energy as the process proceeds (Fig. 69). The more rapid annealing at 40°C after irradiation at -120°C than at 40°C in the reactor can be attributed to the fact that many irradiation-produced defects are present in the former case before the annealing begins, whereas for the in-pile annealing the defects are produced gradually during the irradiation.

Flux Dependence

In-pile measurements have been made of the decrease in resistivity at about 40°C in three facilities, Holes 1768, C, and 52, in the Graphite Reactor. The fast-neutron fluxes in Holes C and 52 are thought to be about the same (approximately 3×10^{11} neutrons $\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$). However, in Hole 1768 the sample lies at the center of a hollow fuel element, and the fast flux is expected to be several times greater than in Holes C and 52. In spite of the expected flux differences, the

resistivity curves for the irradiations in Holes 1768, C, and 52 were found to superimpose quite well on one another (Fig. 71).

In order to explore further the question of flux dependence, it was decided to perform an interrupted irradiation experiment, whereby the sample is withdrawn to the edge of the reactor and measurements continued with the sample in its new location. The results are shown in Fig. 72. The rate of decrease in resistivity is sharply reduced when the sample is removed from the high-flux portion of the reactor. However, when the sample

Fig. 71. In-Pile Measurements of Change in Resistivity of Cu-Al (15 at. % Al) upon Irradiation in Three Facilities in the Graphite Reactor.

Fig. 72. Interrupted Irradiation Experiment. Cu-Al (15 at. % Al).

is reinserted, the rapid decrease in resistivity is resumed.

Irradiation of Quenched Samples

It has been previously noted^{3,4} that an additional resistivity of about $0.5 \mu\text{ohm-cm}$ is retained upon quenching from 450°C . This quenched-in resistivity anneals out in about 10^4 min at 45°C . Also, the final value after quench-annealing usually lies somewhat below the value before quenching. It is of interest to investigate how the annealing of quenched samples is affected by irradiation. In Fig. 73 annealing curves are compared for two samples that were quenched from 450°C . In both cases an additional resistivity of $0.45 \mu\text{ohm-cm}$ resulted from the quenching. The unirradiated sample was then annealed at 45°C , and measurements were made during the annealing (open circles). The other quenched sample was irradiated at -128°C for three weeks, which introduced only $0.01 \mu\text{ohm-cm}$. Following the irradiation, this sample was also annealed at 45°C . Figure 73 shows that the irradiation at -128°C affects the quench-annealing in two ways. First, the annealing of the irradiated sample occurs more rapidly in the early portion of the curve. Second, a type of stabilization takes place in the irradiated sample whereby even after prolonged holding at 45°C only one-half of the quenched-in resistivity is annealed out. It was found necessary to raise

Fig. 73. Effect of Irradiation at -128°C on the Annealing of Quenched Cu-Al (15 at. % Al). Both samples were quenched from 450°C .

the temperature above 100°C in order to realize a further decrease in resistivity, and only a prolonged heating at 195°C would induce the resistivity of the irradiated sample to return to the value it had before the quenching.

The irradiation-induced stabilization of the quenched-in resistivity was also investigated by doing isochronal annealing experiments. The results are shown in Fig. 74, where curves 3 and 4 correspond to the two curves in Fig. 73. The annealing of the sample that was quenched and irradiated (curve 4) is more rapid at lower temperatures, but after about one-half of the quenched-in resistivity is recovered the annealing becomes more difficult. The isochronal annealing curves for an annealed sample (curve 1) and a sample previously irradiated at -120°C (curve 2) are shown for comparison. These curves and the peak that occurs at about 310°C have been discussed previously.^{2,4} It appears that the effect of the pretreatments is lost upon raising the temperature above about 250°C .

Since the prior irradiation at -128°C has the effect of stabilizing a portion of the quenched-in resistivity, the question arises as to the effect of irradiation at 45°C on the quench-annealing.

Fig. 74. Isochronal Annealing ($t = 30$ min) Following Several Previous Treatments. All measurements made at liquid nitrogen temperature. The point labeled $\Delta(Q)$ refers to the value after the quenching but before the irradiation.

This is shown in Fig. 75. Out of the reactor, the annealing at 45°C after quenching proceeds as shown in curve 3, whereas the corresponding annealing after quenching at this temperature *in the reactor* is given by curve 4. Thus, when the quench-annealing goes on in the reactor no stabilization takes place. The quench-annealing in the reactor (curve 4, Fig. 75) at 45°C appears to be roughly equivalent to the combined effects of the quench-annealing that would have occurred at 45°C in the absence of the irradiation (curve 3) plus the decrease in resistivity upon irradiation at 45°C for an annealed (not quenched) sample (curve 1).

Changes in Specific Volume upon Neutron Irradiation

The observation of changes in specific volume of Cu-Al (15 at. % Al) upon irradiation may help to evaluate the relative merits of several suggestions² that have been made as to the nature of the process that causes the decrease in resistivity upon irradiation. On the one hand, the decrease in resistivity may be due to short-range ordering or, alternatively, to local segregation (such as is involved in Guinier-Preston zone formation) induced by the irradiation. A second possibility is that a nonequilibrium number of vacancies is retained during cooling and the decrease corresponds to the annealing out of these vacancies upon irradiation.

Fig. 75. Isothermal Annealing at 45°C Following Several Previous Treatments. Cu-Al (15 at. % Al).

If the vacancy-annealing mechanism were correct, the fractional change in specific volume corresponding to the annealing of vacancies during the irradiation would be given by⁵⁻⁷

$$\frac{\Delta v}{v} = -(1 - 3\alpha) C, \quad (3)$$

where C is the concentration of vacancies being annealed and α is the relative linear contraction of the lattice about the vacancy. In contrast, a lattice parameter measurement is not cognizant of the fact that a lattice site is vacant but is only sensitive to the lattice contraction about the vacancy. Thus, the fractional change in lattice parameter upon the annealing of a concentration C of vacancies is given by

$$\frac{\Delta a_0}{a_0} = \alpha C. \quad (4)$$

Theoretical estimates^{8,9} for pure copper give $\alpha \approx 0.2$.

Specific volume measurements on single crystals of Cu-Al have been made by the method of hydrostatic weighing. The technique employed is essentially the same as that previously described^{5,6} in connection with measurements on Au-Cd upon quenching. A special irradiation capsule is being used, which permits a resistivity sample to be irradiated in the same location and at the same time as the specific volume sample. Since the decrease in resistivity observed upon irradiation at 100°C is almost as large as that observed at 45°C (Fig. 64), it was decided to irradiate the samples at 100°C. Shorter exposure times are required at this temperature, which reduces the handling problem upon removing the samples from the reactor. Control samples for specific volume and resistivity measurements were held at 100°C outside the reactor for the same periods as the irradiated samples. The

⁵W. J. Sturm and M. S. Wechsler, *Solid State Semiann. Prog. Rep. Aug. 30, 1955*, ORNL-1945, p 76.

⁶W. J. Sturm and M. S. Wechsler, *J. Appl. Phys.* **28**, 1509 (1957).

⁷R. O. Simmons and R. W. Balluffi, *J. Appl. Phys.* **30**, 1249 (1959).

⁸C. W. Tucker and J. B. Sampson, *Acta Met.* **2**, 433 (1954).

⁹L. Tewordt, *Phys. Rev.* **109**, 61 (1958).

results of the resistivity and specific volume measurements on the irradiated samples are shown in Fig. 76. The control resistivity sample underwent a decrease of less than $0.01 \mu\text{ohm-cm}$, whereas the irradiated sample decreased about $0.14 \mu\text{ohm-cm}$. The specific volume measurements upon irradiation, shown in Fig. 76, are relative to the control samples. In this way corrections are made for changes produced by the heat treatment at 100°C or changes in the density of the liquid used in making the specific volume measurements. The results indicate that a decrease in resistivity of $0.14 \mu\text{ohm-cm}$ is accompanied by a fractional volume decrease of 2.3×10^{-4} . In the case of pure copper, it has been observed that the specific volume increases slightly upon neutron irradiation¹⁰ at 100°C . With the use of Eq. (3) and the value $\alpha = 0.2$, we find that $C = 0.058\%$ vacancies on the assumption that the decrease in specific volume is due to vacancy annealing. This concentration is smaller than that predicted from the resistivity decrease since, corresponding to the value $1.3 \mu\text{ohm-cm}$ per atomic per cent of vacancies for pure copper,¹¹ we obtain $C = 0.14/1.3 = 0.11\%$.

These considerations emphasize the importance of determining the effect of neutron irradiation on the lattice parameter. From Eq. (4) we find that an increase in lattice parameter of

$$\frac{\Delta a_0}{a_0} = 1.2 \times 10^{-4},$$

which corresponds to $\Delta a_0 = 0.0004 \text{ \AA}$, should accompany the annealing of 0.058% vacancies.

Fig. 76. Changes in Specific Volume and Resistivity upon Irradiation at 100°C .

On the other hand, if the decrease in resistivity were due to short-range ordering or segregation, no new sites would be created, and the relative change in lattice parameter would be equal to one-third of the relative change in volume. Thus, this mechanism predicts a decrease in lattice parameter upon irradiation of $\Delta a_0/a_0 = -0.8 \times 10^{-4}$ or $\Delta a_0 = -0.0003 \text{ \AA}$. Unfortunately, these changes in lattice parameter are on the border line of the present experimental precision, and the results of a preliminary attempt to measure changes in lattice parameter were inconclusive. It is planned to repeat the experiment.

Gamma Irradiation of Cu-Al

Resistivity measurements have been made on a Cu-Al (15 at. % Al) sample as a function of exposure to Co^{60} gamma radiation at about 18°C in the canal storage facility at the Graphite Reactor. A decrease in resistivity was observed (Fig. 77). A comparison may be made of the effects of the two types of radiation by extrapolating the neutron data to 18°C with the aid of Fig. 68. The normalized decay curves are shown in Fig. 78, where the points represent the experimental data and the curves indicate the fit to second-order kinetics [Eq. (2)]. These results indicate that, as regards the magnitude of the decrease in resistivity and the shape of the decay curve, the effect of gamma irradiation on Cu-Al (15 at. % Al) is quite similar to the effect of neutron irradiation.

¹⁰R. R. Coltman, personal communication.

¹¹P. Jongenburger, *Phys. Rev.* **90**, 710 (1953); *Appl. Sci. Research* **B3**, 237 (1953).

Fig. 77. Change in Resistivity of Cu-Al (15 at. % Al) vs Time of Exposure to Co^{60} Gamma Rays at 18°C .

Fig. 78. Normalized Decay Curves for Gamma and Neutron Irradiation of Cu-Al (15 at. % Al) at 18°C. The theoretical curves illustrate the fit to Eq. (2).

The times for half-decay are $\tau_\gamma = 6.8 \times 10^4$ min and $\tau_n = 5.3 \times 10^3$ min for the gamma and neutron exposures, respectively. The relative effectiveness of the two types of radiation may be estimated from the fluxes $\phi_\gamma = 5 \times 10^{11}$ photons·cm⁻²·sec⁻¹ (refs 12, 13) and $\phi_n = 3 \times 10^{11}$ neutrons·cm⁻²·sec⁻¹, and from the cross sections for primary collisions $\sigma_\gamma = 0.12 \times 10^{-24}$ cm² (ref 14) and $\sigma_n = 3.5 \times 10^{-24}$ cm². Thus, the fractional number of primaries necessary to produce half decay as a result of the gamma irradiation is $\phi_\gamma \sigma_\gamma \tau_\gamma = 2.5 \times 10^{-7}$. The corresponding number of primaries produced by the neutron irradiation is $\phi_n \sigma_n \tau_n = 3.3 \times 10^{-7}$. We are therefore led to the conclusion that each gamma-photon collision is approximately as effective as each neutron collision. This is quite surprising in view of the fact that each neutron primary is thought to produce about 100 secondary displacements, whereas each gamma primary rarely produces even one secondary displacement.¹⁴

IRRADIATION EFFECTS ON THE PRECIPITATION REACTION IN Ni-Be

In contrast to the case of Cu-Al, the nature of the metastability illustrated in Fig. 63 is quite well known for Ni-Be. The solubility of beryllium

in nickel increases with temperature from 2 at. % at 400°C to 15.3 at. % at 1157°C. Thus, when a 15 at. % Be sample is cooled rapidly from about 1150°C to room temperature, the solid solution becomes supersaturated with beryllium. Therefore, the decrease from B' to C' in Fig. 63 corresponds to the precipitation of beryllium in order that the amount remaining in solid solution be characteristic of equilibrium at the temperature T_0 . However, in the Ni-Be case it is not necessary to irradiate the alloy in order to bring about the decrease from B' to C' . The normal heat treatment consists of aging the supersaturated solid solution at 300–550°C, whereupon the excess beryllium precipitates out in the form of the nonmagnetic intermetallic compound NiBe, containing 50 at. % Be.

It is of interest to investigate how radiation affects this precipitation reaction. Previous work has indicated^{15,16} that the precipitation is accelerated when the alloy is aged at 300°C in the reactor, although the effect is somewhat more complex upon aging in the laboratory following irradiation at 35°C. A further aspect of the problem is the effect of the irradiation when the alloy is in the aged condition. This question arises in connection with the work of Boltax¹⁷ on the effect of radiation on Cu-Fe alloys, where it was suggested that high-energy particle irradiation can cause re-solution of precipitate particles. This possibility was tested for Ni-Be by irradiating six Ni-Be (15 at. % Be) samples in the aged condition for four weeks at ambient pile temperature in Hole 1968 of the Graphite Reactor. The results of hardness, resistivity, and Curie temperature measurements are shown in Table 14. Samples 1–4 were aged sufficient times at temperatures of 400, 450, 500, and 550°C to produce maximum hardness, whereas samples 5 and 6 were over-aged to give somewhat smaller hardness values. The heat treatment times and temperatures may be compared with the hardness curves given in Fig. 79. It may be seen from Table 14 that the

¹⁵R. H. Kernohan et al., *Solid State Ann. Prog. Rep.* Aug. 31, 1957, ORNL-2413, p 22; R. H. Kernohan, A. B. Lewis, and D. S. Billington, *Solid State Semian. Prog. Rep.* Aug. 30, 1956, ORNL-2188, p 92.

¹⁶R. H. Kernohan, D. S. Billington, and A. B. Lewis, *J. Appl. Phys.* 27, 40 (1956).

¹⁷A. Boltax, *Am. Soc. Testing Materials Spec. Tech. Publ. No. 208*, p 183 (1957); *Bull. Am. Phys. Soc.* 4, 136 (1959).

¹²G. W. Leddicotte, personal communication.

¹³C. D. Bopp and O. Sisman, *Nucleonics* 14, 46 (January 1956).

¹⁴O. S. Oen and D. K. Holmes, *J. Appl. Phys.* 30, 1289 (1959).

Table 14. Changes in Hardness, Resistivity, and Curie Temperature upon Irradiation of Aged Ni-Be Alloys

Sample No.	Preirradiation Heat Treatment		H , Hardness (DPH)			ρ , Resistivity ($\mu\text{hm-cm}$)			θ_c , Curie Temperature ($^{\circ}\text{C}$)			Change in Amount of Be in Solid Solution (at. %)
	Time (hr)	Temperature ($^{\circ}\text{C}$)	Before Irradiation	After Irradiation	ΔH	Before Irradiation	After Irradiation	$\Delta\rho$	Before Irradiation	After Irradiation	$\Delta\theta_c$	
1	400	400	605	617	12	24.95	24.91	-0.04	214.4	213.8	-0.6	0.03
2	24	450	627	602	-25	25.31	25.21	-0.10	219.2	219.5	0.3	-0.015
3	2	500	620	620	0	25.70	25.54	-0.16	217.4	218.6	1.2	-0.06
4	0.25	550	614	610	-4	25.68	25.70	0.02	215.3	215.0	-0.3	0.015
5	40	500	460	456	-4	19.14	19.01	-0.13	264.4	264.7	0.3	-0.015
6	5	550	431	442	11	19.50	19.58	0.08	256.7	256.7	0	0

Fig. 79. Changes in Hardness upon Aging of Ni-Be (15 at. % Be).

irradiation at ambient pile temperature (35°C) had no significant effect on the aged alloys. Thus, no re-solution was observed to take place as a direct effect of the bombardment at this temperature.

This result is similar to the effect of radiation at 35°C on the alloy in the solution-annealed and quenched (from 1125°C) state, in which a negative result was also obtained. Thus, it seems that no significant amount of atomic rearrangement takes place in Ni-Be at 35°C even in the presence of the neutron flux. However, when the temperature of the sample is raised to the heat-treatment temperatures (300 – 550°C), the effect of the prior irradiation at 35°C may be observed. This is illustrated in Fig. 80, where it is seen that the prior irradiation has the effect of enhancing the

Fig. 80. Effect of Irradiation at 35°C on the Aging of Ni-Be as Determined by Curie Temperature Measurements. All samples were solution-annealed at 1125°C and quenched.

initial precipitation, although the precipitation in the irradiated samples is more sluggish in the later stages of the reaction. This effect is qualitatively quite similar to the results of the corresponding experiment on Cu-Al shown in Fig. 73.

The effect of neutron irradiation has also been studied by comparing the aging of unirradiated samples at 300°C with the aging of samples held at the same temperature in the reactor. In this case no retardation of the precipitation reaction is observed, as can be seen in Fig. 81. In addition, Fig. 81 shows that the behavior of Cu-Al under these circumstances also is quite similar

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to that of Ni-Be. Thus, a correspondence between temperatures for the two alloys may be given, as shown in Table 15.

These experiments indicate that in comparing the results of irradiations on different alloys due consideration must be given to the temperature ranges in which the pertinent reactions take place. In particular, it may frequently occur that, although no changes in properties take place at the irradiation temperature (as in the case of Ni-Be at 35°C or Cu-Al at -120°C), the irradiation effect may not be absent. It may merely be latent, and upon subsequent raising of the temperature, the irradiation effect may be released.

IRRADIATION AND QUENCHING EFFECTS ON AN Ni-Cu ALLOY

Unlike either Cu-Al or Ni-Be, the Ni-Cu system exhibits a continuous range of solid solubilities.

For this reason a study of irradiation effects on Ni-Cu alloys has been undertaken.

Preliminary measurements have been made of the effect of neutron irradiation and quenching on the Curie temperature and electrical resistivity of an Ni-Cu alloy containing about 28 at. % copper. It is known¹⁸ that the Curie temperature of nickel decreases linearly with the atomic percentage of copper that is alloyed with it. Thus, an increase in the Curie temperature of an Ni-Cu sample of a given bulk composition is a measure of a decrease in the amount of copper in solid solution with the nickel.

The effect of irradiation in Hole 1867 at about 20°C for four weeks is shown in Table 16. It is seen that an increase in Curie temperature of 3.6°C is observed upon irradiation. According to the work of Torkar and Götz,¹⁹ the slope of the Curie temperature-composition curve is 10.7°C per atomic per cent copper. Thus, the irradiation may be considered to remove 0.34 at. % Cu from

Fig. 81. Annealing After Quenching In and Out of the Reactor for Cu-Al (15 at. % Al) and Ni-Be (15 at. % Be).

¹⁸V. Marian, *Ann. Phys.* 7, 459 (1937).

¹⁹K. Torkar and H. Götz, *Z. Metallk.* 46, 374 (1955).

Table 15. Corresponding Temperatures for Cu-Al and Ni-Be

Alloy	T_Q (°C)	T_I (°C)	T_A (°C)
Cu-Al	450	-120	45
Ni-Be	1125	35	300

T_Q = quenching temperature.

T_I = irradiation temperature at which no effects are seen.

T_A = reaction temperature for aging or annealing at which irradiation effects are observed.

Table 16. Changes in Curie Temperature and Resistivity of an Ni-Cu (28 at. % Cu) Alloy upon Four Weeks' Irradiation at About 20°C

	θ_c , Curie Temperature (°C)			ρ , Resistivity (μohm-cm)		
	Before Irradiation	After Irradiation	$\Delta\theta_c$	Before Irradiation	After Irradiation	$\Delta\rho$
Irradiated samples	48.4	52.0	3.6	40.92	40.35	-0.57
Control samples	49.0	48.2	-0.8	40.87	40.91	0.04

solid solution with the nickel. The resistivity decrease upon irradiation is more difficult to interpret in this fashion. However, if one makes the assumption that the resistivity decrease is due, effectively, to the removal of copper from solid solution, then the curve of resistivity vs composition given by Smithells²⁰ may be used to evaluate the loss of copper. In the region of 0 to 30 at. % Cu, one finds that the resistivity vs composition is linear, corresponding to a slope of 1.3 $\mu\text{ohm-cm}$ per atomic per cent copper. Thus, a decrease of 0.57 $\mu\text{ohm-cm}$ corresponds to a decrease of 0.44 at. % Cu.

The effect of quenching from 600 and 700°C is shown in Table 17, where it is seen that a decrease in Curie temperature takes place. It would appear that at higher temperatures the equilibrium configuration is more random and that the more random structure is retained upon quenching.

The preliminary results on this alloy are in accord with the work of Ryan, Pugh, and Smoluchowski,²¹ who conclude from magnetic susceptibility measurements on alloys of higher copper concentration that there is a tendency toward segregation as the temperature is lowered. The equilibrium degree of segregation is not achieved upon cooling, and the irradiation enhances the approach to the more segregated condition characteristic of room temperature.

PRECIPITATION OF CARBON IN ALPHA-IRON

(In Collaboration with

D. O. Thompson and V. K. Paré)

As is discussed above, two general mechanisms may be devised to explain the irradiation effects on the alloys already mentioned: (1) the injection of nucleation sites which facilitate the nucleation of the reaction product and (2) the production of vacancies which aid in the diffusion necessary to bring about the difference in composition or atomic arrangement between the parent and product structures. But the latter mechanism applies directly only if the solute diffuses as a result of solute-vacancy interchanges and, thus, only if the solute is dissolved *substitutionally* in the solid

Table 17. Changes in Curie Temperature upon Quenching Ni-Cu (28 at. % Cu)

Data are the averages for two samples

Condition	θ_c (°C)	$\Delta\theta_c$ (°C)
Slow cooled	48.2	
Quenched from 600°C	45.7	-2.5
Quenched from 700°C	41.0	-7.2

solution. However, many precipitation reactions exist in which the solute, whose motion controls the formation of the precipitate, is located on *interstitial* sites. The most prominent example of this type of precipitation reaction is the formation of carbides and nitrides in alpha-iron. Therefore, it appears of value to investigate the effect of radiation on the precipitation of carbon in alpha-iron.

A convenient and sensitive measure of the amount of carbon remaining in solid solution during the precipitation is the damping capacity of a torsion pendulum in which the sample wire is used as the suspension.²² Iron-carbon wires²³ of 14 mils diameter were recrystallized at 600°C from the cold-drawn condition to reveal an average grain diameter of approximately 2 mils. The sample wire was solution-annealed in a helium atmosphere for several minutes at 720°C and rapidly quenched into water. The damping peak (Fig. 82) was then obtained by measuring the internal friction, Q^{-1} , as a function of temperature, where Q^{-1} is defined by the expression

$$Q^{-1} = \frac{1}{\pi f t} \ln \frac{A(0)}{A(t)}$$

and where f is the frequency of the pendulum and $A(0)$ and $A(t)$ are the amplitudes at time $t = 0$ and time t . The peak height is a measure of the amount of carbon in solid solution (0.008 wt %),

²⁰C. J. Smithells, *Metals Reference Book*, vol II, p 675, Interscience Publishers, Inc., New York, 1955.

²¹F. M. Ryan, E. W. Pugh, and R. Smoluchowski, *Bull. Am. Phys. Soc.* 4, 137 (1959).

²²Cf. C. A. Wert, "The Metallurgical Use of Anelasticity," *Modern Research Techniques*, Am. Soc. Metals, 1954.

²³We are indebted to Professor C. Wert for providing carburized wires of 30 mils diameter. We wish to thank also J. H. Erwin and G. D. Goldston for drawing the wires from 30 to 14 mils.

and the peak temperature indicates that the redistribution of interstitial carbon atoms, stimulated by the application of a cyclic torsional stress, is accomplished with an average jump time at 36°C of $1/2\pi f = 0.28$ sec.

Since the peak temperature does not change as the carbon precipitates, the amount of carbon remaining in solid solution is determined by measuring the internal friction at the peak temperature as a function of time at the aging temperature. The internal friction at 37°C is shown in Fig. 83 as a function of aging time at 37°C for a sample that was quenched from 720°C. It is seen that there is an incubation time at 37°C of about 10^4 min. Theoretical analyses^{24,25} of the kinetics of growth of precipitate particles have indicated that the fractional amount of untransformed material, f ,

Fig. 82. Damping Peak of Carbon in Alpha-Iron.

Fig. 83. Internal Friction vs Time for Alpha-Iron Sample Quenched from 720°C. Aging temperature is 37°C.

should be given by an expression of the form

$$f = \exp \left(-\frac{t}{\tau} \right)^n, \quad (6)$$

where the relaxation time, τ , is characteristic of the aging temperature and the growth exponent, n , is characteristic of the shape of the precipitate particle. A test of the fit to Eq. (6) is shown in Fig. 84, from which the value of n is found to be 1.44. This agrees with the value $n = 1.49$ given by Wert²⁶ for an alloy containing a somewhat higher concentration of carbon.

No measurements on irradiated samples have been made as yet.

²⁴W. A. Johnson and R. F. Mehl, *Trans. Am. Inst. Mining Met. Engrs.* 135, 416 (1939).

²⁵C. Zener, *J. Appl. Phys.* 20, 950 (1949).

²⁶C. Wert, *J. Appl. Phys.* 20, 943 (1949).

Fig. 84. Test of the Fit of Precipitation Kinetics of Carbon in Alpha-Iron to the Expression $f = \exp (-t/\tau)^n$.

**MARTENSITIC TRANSFORMATIONS.
THE EFFECT OF NEUTRON IRRADIATION
ON THE CUBIC-TETRAGONAL AND
CUBIC-ORTHORHOMBIC TRANSFORMATIONS
IN Au-Cd**

There are two martensitic transformations that take place in the beta-phase Au-Cd alloy near the equiatomic composition. The 47.5 at. % Cd alloy transforms upon cooling at about 60°C from the cubic to an orthorhombic structure,²⁷ whereas the 50 at. % alloy transforms upon cooling at about 30°C to a structure that has been designated as tetragonal.²⁸ In both cases the reverse transformations upon heating occur at higher temperatures. Because the transformations occur near room temperature, it has been found convenient to experiment with these alloys in order to learn more about the nature of martensitic transformations.²⁹ In addition, a detailed analysis of the crystallography of the cubic to orthorhombic phase change has been given.³⁰ Also, it has been found that marked changes in the transformations may be brought about by quenching.³¹ The temperature for the cubic to tetragonal transformation is reduced about 6°C upon quenching from 442°C. Also, the transformation for the 47.5 at. % Cd alloys goes to the tetragonal phase upon quenching from 410°C instead of the orthorhombic phase.

The experiments on the effect of quenching on the transformations give rise to the question of the effect of irradiation. Therefore, an experiment was performed in which single crystals of the 47.5 and the 50 at. % Cd alloys were irradiated in Hole A of the Graphite Reactor. The samples were mounted inside a heater, along with a dummy sample to which a thermocouple was soldered in order to control and monitor the temperatures. The resistivities of the samples were measured by passing a constant direct current through them and feeding to a recorder the amplified output from voltage contacts on the samples. In this way

the samples could be cycled through the transformations and the resistivity-vs-temperature hysteresis loops recorded while the samples were in the reactor. In order to obtain conveniently the lower temperatures needed for the cubic to tetragonal transformation, the experiment was done in the wintertime, and most of the hysteresis loops were obtained when the reactor was down.

Figures 85 and 86 show the hysteresis loops measured before and after exposure to an integrated neutron flux of 10^{18} neutrons/cm². It may be seen that the effects of the radiation are not extensive. There is a slight indication of a decrease in transformation temperature and possibly a decrease in resistivity upon irradiation. However,

Fig. 85. The Effect of Neutron Irradiation on the Transformation in Au-Cd (50 at. %). Temperature of irradiation 25–30°C. In-pile measurements with reactor down.

Fig. 86. The Effect of Neutron Irradiation on the Transformation in Au-Cd (47.5 at. % Cd). Temperature of irradiation 25–30°C. In-pile measurements with reactor down.

²⁷A. Bystrom and K. E. Almin, *Acta Chem. Scand.* 1, 76 (1947).

²⁸W. Köster and A. Schneider, *Z. Metallk.* 32, 156 (1940).

²⁹L. C. Chang and T. A. Read, *Trans. Am. Inst. Mining Met. Engrs.* 191, 47 (1951).

³⁰D. S. Lieberman, M. S. Wechsler, and T. A. Read, *J. Appl. Phys.* 26, 473 (1955).

³¹M. S. Wechsler and T. A. Read, *J. Appl. Phys.* 27, 194 (1956).

it would appear advisable to repeat the experiment using higher flux levels and temperatures of irradiation before any conclusions are drawn.

THE THEORY OF MARTENSITIC TRANSFORMATIONS

The Generalized Lattice Invariant Shear and the Degeneracy of Solutions for the Cubic to Tetragonal Transformations.³² M. S. Wechsler. — The theory of the crystallography of martensitic transformations³³ is extended in terms of generalized elements for the lattice invariant shear. The degeneracy of solutions for the undistorted plane, the orientation relation, and the macroscopic change of shape is examined analytically for the cubic to tetragonal transformation. The criteria for *K*-degeneracy and *g*-degeneracy are developed and compared with those given by Christian³⁴ as a result of a geometrical treatment. Existence conditions for real solutions are also developed in terms of the generalized theory.

The Crystallography of the Austenite-Martensite Transformation. The {111} Shear Solutions.³⁵ M. S. Wechsler, T. A. Read,³⁶ and D. S. Lieberman.³⁶ — The graphical method^{37,38} is applied to the austenite-martensite transformation. The undistorted planes are determined for the lattice invariant shear on the (111) austenite plane. The solutions are discussed in terms of their degeneracy and their applicability to the formation of (225) martensite.

³² Abstract of paper to be published in *Acta Met.*

³³ M. S. Wechsler, D. S. Lieberman, and T. A. Read, *Trans. Am. Inst. Mining Met. Engrs.* **197**, 1503 (1953).

³⁴ J. W. Christian, *J. Inst. Metals* **84**, 386 (1955).

³⁵ Abstract of paper to be published in *Trans. Met. Soc. AIME*.

³⁶ University of Illinois.

³⁷ D. S. Lieberman, T. A. Read, and M. S. Wechsler, *J. Appl. Phys.* **28**, 532 (1957).

³⁸ D. S. Lieberman, *Acta Met.* **6**, 680 (1958).

SEMICONDUCTOR STUDIES

DISORDERED REGIONS IN SEMICONDUCTORS

B. R. Gossick¹

The following has been published in the open literature.

Disordered Regions in Semiconductors Bombarded by Fast Neutrons.² B. R. Gossick. — The width and depth of the potential wells surrounding disordered regions in neutron-irradiated, *n*-type germanium and extrinsic silicon are estimated. Numerical examples of well dimensions for a wide range of sample characteristics are presented. Some effects of disordered regions, e.g., (a) scattering of conduction electrons, (b) absorption of holes, and (c) polarizability are discussed.

FERMI LEVEL SPECTROMETRY

J. W. Cleland

J. H. Crawford, Jr.

It has previously been suggested³ that nuclear doping might be employed to alter the position of the Fermi level or Fermi energy ζ in a semiconductor so that the energy structure and nature of radiation-produced defects might be examined. H. C. Schweinler⁴ has shown that the average recoil energy expected from thermal-neutron capture in germanium is ~ 182 ev; hence, each thermal-neutron absorption probably results in the formation of an interstitial germanium atom, prior to any transmutation effects.

The number of thermal-neutron absorptions (and presumably recoils) in germanium is ~ 0.108 *nut*, where *nut* is the total incident thermal-neutron flux.⁴ For every neutron absorbed, 0.098 As⁷⁵, 0.012 Se⁷⁷, and 0.304 Ga⁷¹ atoms are ultimately formed. The total contribution of donor electrons from radioactive decay to As and Se is 0.122 electron per thermal neutron absorbed with a half life of 82 min for the As⁷⁵, 12 hr for Ge⁷⁷, and 39 hr for Se⁷⁷, where this latter effect produces twice 0.012 or 0.024 electron. This total contribution of 0.122 electron is accompanied by the

production, with a 12-day half life, of 0.304 acceptor hole per thermal-neutron absorption as the result of the formation of Ga⁷¹. The end result, after five or six half lives (60–72 days), is a net decrease of 0.182 electron per thermal neutron absorbed.

Preliminary experiments have been conducted in the "thermal bump" position (approximately 1 ft inside the graphite), using the foil slot of Hole W-13, thermal column, Brookhaven National Laboratory Reactor. This facility was listed⁵ as having a thermal-neutron flux of $\sim 1 \times 10^{11}$ *nv*, with a cadmium ratio of ~ 3000 . This reactor was reloaded in 1957, and the central-core thermal flux increased about a factor of 4. The size of the active lattice was reduced by this reloading; hence, the cadmium ratio at the "thermal bump" position would be expected to be somewhat larger. A general rule of thumb has been that a cadmium ratio of 30 means an equal concentration of thermal-energy and higher-energy (epithermal and higher) neutrons. Thus, a cadmium ratio of 6000 would mean 200 thermal-energy neutrons per one of epithermal energy or higher. The reloading would also be expected to provide $\sim 4 \times 10^{11}$ *nv* of thermal-energy neutrons at the specified position.

The experimentally determined⁶ conduction electron removal rate for *n*-type germanium in a fission spectrum is ~ 3.2 per incident fast (damaging) neutron. Thus, 3.2/200 displacements might be expected per incident thermal-energy neutron in the above position. The initial electron concentration of several samples was obtained by a measurement of the Hall coefficient. The samples were enclosed in a boral container to minimize the thermal-neutron dosage and were irradiated. They were only very mildly radioactive upon return, in contrast to unshielded specimens; hence, the boral is apparently very effective in attenuating the thermal flux. The final electron concentration after irradiation was within 90% of the value that was calculated under the assumption

¹Department of Physics, Arizona State University, Tempe; consultant to the Solid State Division.

²B. R. Gossick, *J. Appl. Phys.* 30, 1214–18 (1959).

³J. W. Cleland *et al.*, *Solid State Semiann. Prog. Rep.* Feb. 28, 1955, ORNL-1852, p 17.

⁴H. C. Schweinler, *J. Appl. Phys.* 30, 1125–26 (1959); see also abstract, this report.

⁵D. J. Hughes, *Pile Neutron Research*, p 68, Addison-Wesley, Cambridge, Mass., 1953.

⁶J. H. Crawford and J. W. Cleland, *Progress in Semiconductors*, vol 2, p 75, Wiley, New York, 1957.

of 3.2 electrons removed per incident fast (damaging) neutron and a fast (damaging) flux of 1/200 of the thermal-neutron flux.

The actual thermal-energy neutron flux in the foil slot was also determined by experiment. The original electron concentration was obtained for several samples by a measurement of the Hall coefficient. The final electron concentration, after complete radioactive decay and vacuum anneal at 450°C (to restore any displaced atoms) gave the final net number of transmuted atoms and was therefore employed to ascertain the thermal-neutron flux incident on the sample. The average thermal-energy neutron flux was 3.4×10^{11} *nv*, in good agreement with the enhanced thermal flux expected as a result of the reloading.

The net result of a typical experiment can be summarized as follows. An *n*-type sample with an initial electron concentration of 4.9×10^{14} cm^{-3} as determined at 77°K was irradiated for 3 hr in a flux of 3.54×10^{11} thermal neutrons for a total dosage of 3.82×10^{15} *nv*. This resulted in 4.13×10^{14} thermal-neutron captures, 5.04×10^{13} electrons contributed by As and Se, 6.13×10^{13} electrons removed by epithermal or higher energy neutron effects, and 1.25×10^{14} electrons removed by the introduction of Ga. The final electron concentration expected from the fast-neutron damage and transmutation effects was 3.54×10^{14} cm^{-3} , whereas the actual final electron concentration was 1.0×10^{14} cm^{-3} . Thus, 2.54×10^{14} electrons/ cm^3 were evidently removed from the conduction band by the 2.38×10^{14} thermally activated germanium atoms that were displaced by recoil but did not later transmute to As, Se, or Ga. Thus, $1.0 (\pm 10\%)$ electron was removed from the conduction band for each germanium atom that absorbed an incident thermal-energy neutron, probably recoiled to an interstitial position, but did not subsequently contribute or remove electrons from conduction as a result of transmutation. This result has been verified for quite a few samples over a wide range of initial carrier concentrations. It has also been verified for a sample that contained a large number of defects previously introduced by fast neutrons.

The effect of fast neutrons on germanium^{5,7} is to introduce a very inhomogeneous distribution of

defects. The result is that electrons are removed from the conduction band, the sample converts to *p*-type material, and the hole concentration increases to a limiting Fermi level ζ that is ~ 0.125 ev above the valence band. The effect of Co^{60} gamma rays, however, is to introduce a random distribution of defects that are probably simple interstitial-vacancy pairs. Here the sample again converts to *p*-type, but the limiting Fermi level ζ is much higher, ~ 0.26 ev, above the valence band. Extended irradiation of originally *n*-type germanium by Co^{60} gamma rays, after conversion to *p*-type, does not increase the hole concentration above that represented by the limiting Fermi level value near the middle of the forbidden band.

A result similar to the case for Co^{60} gamma rays has also been observed for samples when germanium atoms were displaced by the recoil resulting from thermal-neutron absorption. The electron concentration was decreased to essentially intrinsic conditions; however, no evidence of conversion to *p*-type was obtained, even though the samples were heavily irradiated. These results would also indicate that the limiting Fermi level position was near the middle of the forbidden band for those acceptors resulting from displaced germanium atoms that recoiled following thermal-neutron absorption.

The original experiments on nuclear doping³ were conducted at 77°K. The position of the Fermi level in germanium, however, is a function of both the extrinsic carrier concentration and the temperature; and the Fermi level value at 77°K for a sample with only 10^{12} electrons/ cm^3 is still only ~ 0.095 ev below the conduction band. It is therefore impossible to sweep the Fermi level across the expected energy-level position of fast-neutron- or Co^{60} -gamma-ray-introduced levels (0.18–0.23 ev) at 77°K. The behavior of those displaced germanium atoms that recoil upon thermal-neutron absorption is also a hindrance, since the electron concentration is altered more by this effect than by subsequent transmutation.

It has therefore been necessary to conduct the experiments at dry-ice temperature, at which the Fermi level can be altered over the expected region of energy levels introduced by fast neutrons. It has also been necessary to introduce the potential transmutations by irradiation and then vacuum anneal the sample at 450°C to restore those displaced germanium atoms that recoiled upon thermal-neutron absorption. It has

⁷J. H. Crawford, Jr., and J. W. Cleland, *J. Appl. Phys.* 30, 1204–13 (1959); see also abstract, this report.

finally been necessary, then, to introduce the desired number of fast-neutron- or Co^{60} -gamma-ray-produced defect states subsequent to the above operations.

Figure 87 is a plot of the log conductivity at 195°K vs hours after irradiation of three *n*-type samples of germanium that were handled in the manner outlined above. All three samples were

Fig. 87. Log Conductivity vs Hours After Irradiation with Thermal Neutrons of Three *n*-Type Germanium Specimens.

irradiated in the ORNL LITR rabbit facility, position A-6, for 2 hr, for an estimated total thermal-neutron dosage of 7.2×10^{16} nvt, which should ultimately result in a net carrier concentration decrease of 1.4×10^{15} electrons/cm³. Sample I was exposed to 6×10^{16} Co^{60} gamma rays, which should introduce $\sim 6 \times 10^{13}$ defect states at about 0.2 ev below the conduction band. Sample II was exposed to $\sim 10^{14}$ fast neutrons in a fission spectrum, which should introduce $\sim 3.2 \times 10^{14}$ defect states at about 0.23 ev below the conduction band. Sample III contained an estimated 10^7

dislocations/cm² that were purposely introduced by plastic deformation at 700°C, followed by rapid quenching.⁸ This sample should have contained dislocation-introduced acceptor levels at 0.18 to 0.20 ev below the conduction band.

The results of Fig. 87 do not indicate any pronounced variation of the conductivity as the Fermi level is lowered by nuclear doping from an original position of ~ 0.15 ev below the conduction band to a final position below the center of the conduction band. Instead, the conductivity decreases rather uniformly until the sample converts to *p*-type. This behavior is not understood at present; however, additional experiments are being considered that should resolve this difficulty. It may be necessary to determine the actual carrier concentration rather than the conductivity. It may also be necessary to vary the temperature to ascertain whether the energy levels in question are occupied at 195°K. Simultaneous recording of the Hall coefficient and resistivity as a function of the temperature should permit a more exact analysis of the position and nature of reactor- or Co^{60} -gamma-ray-introduced defect states during the process of nuclear doping as outlined above.

A further extension of the above techniques is also being considered for certain deep-level impurities that act as acceptor states in germanium. The role of Cu, Ni, and Au, as an example, has received considerable attention.⁹ It should be possible to determine the energy position and electrical behavior of the acceptor states introduced by these materials in a manner exactly analogous to that being considered for radiation-produced levels as outlined above.

NATURE OF BOMBARDMENT DAMAGE AND ENERGY LEVELS IN SEMICONDUCTORS

J. H. Crawford, Jr. J. W. Cleland

The following has been published in the open literature.

Nature of Bombardment Damage and Energy Levels in Semiconductors.¹⁰ J. H. Crawford, Jr., and J. W. Cleland. — The different effects of Co^{60} -gamma-ray

⁸R. A. Logan, G. L. Pearson, and D. A. Kleinman, *J. Appl. Phys.* 30, 885 (1959). This sample was supplied by Dr. R. A. Logan, of the Bell Telephone Laboratories.

⁹W. W. Tyler, *Phys. and Chem. Solids* 8, 59 (1959).

¹⁰J. H. Crawford, Jr., and J. W. Cleland, *J. Appl. Phys.* 30, 1204-13 (1959).

SOLID STATE PROGRESS REPORT

and fast-neutron bombardment on the electrical behavior of germanium are discussed in terms of different local distributions of lattice defects expected for these two types of radiation. For the first of these, which is expected to introduce randomly distributed pairs of interstitials and vacancies, the state at 0.20 ev below the conduction band has been found to increase the concentration of ionized scattering centers on becoming occupied with conduction electrons. This state has been ascribed to a mobile interstitial because of its annealing behavior at moderate temperatures. Energy levels in *p*-type germanium and their annealing behavior are also discussed. In neutron-irradiated, *n*-type germanium the behavior of Hall mobility and the apparent energy distribution of defect levels are discussed in terms of a tentative model for the potential distribution around regions of high local lattice disorder expected to result from neutron bombardment. This model postulates that the disordered region is *p*-type and is surrounded by a negative space-charge region in the *n*-type matrix which insulates it from the matrix. This configuration of electrostatic potential around the disordered region in effect produces an insulating region whose radius is ~ 10 times that of the disordered region itself. The behavior of Hall mobility in irradiated, *n*-type specimens is consistent with the predictions of this model.

THERMAL NEUTRON CAPTURE IN SILICON AND GERMANIUM

H. C. Schweinler

The following has been published in the open literature.

Some Consequences of Thermal Neutron Capture in Silicon and Germanium.¹¹ H. C. Schweinler. — The average value of the kinetic energy of recoil following thermal neutron capture and subsequent gamma-ray emission is 780 ev in silicon and 180 ev in germanium. For every neutron capture in silicon, 0.04 P^{31} atoms (therefore, 0.04 excess electrons) are formed by radioactive decay. For every neutron captured in germanium, 0.098 As^{75} , 0.012 Se^{77} (therefore, 0.122 excess electrons), and 0.304 Ga^{71} atoms (therefore, 0.304 excess holes) are ultimately formed, in this time sequence. Analysis of an experiment of J. W. Cleland on the decay of irradiated, *n*-type germanium gives ~ 1.0 electrons removed from the conduction band per initially recoiling germanium atom.

¹¹H. C. Schweinler, *J. Appl. Phys.* 30, 1125–26 (1959).

RADIATION EFFECTS ON CARRIER RECOMBINATION IN GERMANIUM

O. L. Curtis, Jr. J. W. Cleland
J. H. Crawford, Jr.

The study of the more general aspects of radiation effects in recombination has been completed. The results are summarized in two published papers, abstracts of which appear below.

Radiation-Induced Recombination Centers in Germanium.¹² O. L. Curtis, Jr., J. W. Cleland, and J. H. Crawford, Jr. — An attempt has been made to provide a better understanding of minority carrier recombination processes in irradiated germanium. To this end, studies have been made of the minority carrier lifetime of both *n*- and *p*-type material, following fast-neutron and Co^{60} gamma irradiations. The effect of carrier concentration and temperature has been determined. The primary conclusion drawn from these investigations is that the recombination process is associated with an energy level located 0.20 ev below the bottom of the conduction band. From measurements of the lifetime in *n*-type specimens, the hole capture cross section has been calculated and found to be $\sigma_p = 3 \times 10^{-15} \text{ cm}^2$ and $\sigma_p = 4 \times 10^{-16} \text{ cm}^2$ for neutron- and gamma-induced centers, respectively. If a second, lower-lying level is associated with the second ionization of the defect responsible for recombination, then the effective number of recombination centers is reduced in *p*-type material as the hole concentration is increased, due to this ionization. Such a process is in qualitative agreement with the observed data.

Radiation Effects on Recombination in Germanium.¹³ O. L. Curtis, Jr. — The following properties of recombination centers in germanium are obtained on the basis of lifetime data in conjunction with other information available.

Type of Irradiation	Energy Level Position (ev)	$\sigma_p \text{ (cm}^2\text{)}$	$\sigma_n \text{ (cm}^2\text{)}$
		$\times 10^{-15}$	$\times 10^{-17}$
Co^{60} gamma ray	$E_c - E_r = 0.20$	1.1	
Fission neutron	$E_c - E_r = 0.20$	6	
14-Mev neutron	$E_r - E_v = 0.32$	6	2.2

¹²O. L. Curtis, Jr., J. W. Cleland, and J. H. Crawford, Jr., *J. Appl. Phys.* 29, 1722–29 (1958).

¹³O. L. Curtis, Jr., *J. Appl. Phys.* 30, 1174–80 (1959).

The values of cross section are given for room temperature. The capture probabilities are assumed to be independent of temperature except for the case of gamma irradiation, for which there is apparently a fairly strong variation corresponding to a change in the activation energy of 0.07 ev. The selection of the values given above is not entirely unique. The assumptions made in their determination are discussed. The values given are directly applicable only in the case of *n*-type material, the situation in *p*-type material being more complex.

A preliminary effort is being made to use lifetime measurements in the study of defect annealing in the temperature range above room temperature. The results to date indicate large differences in the annealing behavior, depending on the type of irradiation used and the carrier concentrations of the samples. The effect of various doping agents is being considered.

MONOENERGETIC NEUTRON IRRADIATION OF GERMANIUM

O. L. Curtis, Jr. J. W. Cleland

Experiments using 14-Mev neutrons to irradiate germanium have been completed and the results submitted for publication. The following is an abstract of the article accepted for publication in the *Journal of Applied Physics*.

Monoenergetic Neutron Irradiation of Germanium. O. L. Curtis, Jr., and J. W. Cleland. — A study has been made on 14-Mev neutron-irradiated germanium, using lifetime, Hall, and resistivity measurements to determine the nature of the radiation-induced defects and to compare the damage with that produced by neutrons from a fission spectrum. The electron removal rate in high-resistivity, *n*-type material is $\sim 8 \text{ cm}^{-3}$ per incident neutron/ cm^2 , measured at 77°K. Lifetime measurements have been made on *n*- and *p*-type material. On the basis of simple recombination theory, assuming no variation of capture probabilities with temperature, the results for *n*-type material indicate that a recombination level is located 0.32 ev above the valance band near the center of the energy gap. Assuming an introduction rate of recombination centers equal to one-half the electron removal rate in *n*-type material, the following values of recombination capture cross sections are obtained: $\sigma_n = 2.2 \times 10^{-17} \text{ cm}^2$; $\sigma_p = 6 \times 10^{-15} \text{ cm}^2$, the latter value being correct only within about a factor of two. The ratio of the

cross sections, σ_p/σ_n , which is independent of the method of determining the number of recombination centers, is ~ 300 , indicating that the recombination centers are negatively charged. The lifetime measurements for *p*-type germanium are not so readily analyzed. Possible explanations for observed behavior are discussed.

THERMOELECTRIC POWER IN GERMANIUM

O. E. Schow J. C. Pigg C. C. Robinson

Preliminary measurements of the thermoelectric power have been made before and after irradiation on a 3-ohm-cm sample of *n*-type germanium. The results are shown in Figs. 88–90. Preirradiation measurements indicated that the thermoelectric power was a slowly changing function of temperature in the region of -50°C ; hence, this temperature

Fig. 88. Thermoelectric Sample Ep-9-B. Thermoelectric voltage ($\mu\text{v}/^\circ\text{C}$) vs temperature ($^\circ\text{C}$) before irradiation.

Fig. 89. Thermoelectric Sample Ep-9-B. Thermoelectric voltage ($\mu\text{v}/^\circ\text{C}$) vs temperature ($^\circ\text{C}$) after fast-neutron irradiation of 10^{14} nvt .

Fig. 90. Thermoelectric Sample Ep-9-B. Thermoelectric voltage ($\mu\text{V}/^\circ\text{C}$) vs temperature ($^\circ\text{C}$) after fast-neutron irradiation of 2×10^{14} nvt.

region was chosen for the preliminary irradiation experiment.

The thermoelectric power was found to be a function of ΔT throughout the experiment. After the first irradiation the thermoelectric power decreased but increased after the second irradiation. An increase was expected in both instances because of the lowering of the Fermi level of *n*-type germanium by irradiation.

These results indicate the necessity of more precise measurements of thermoelectric power. In preparation for this, equipment has been constructed, and measurements prior to irradiation have been made.

A sample of approximately 2-ohm-cm germanium was soldered into a threaded copper plug. Six B and S No. 30 gage copper-constantan thermocouples were attached to the germanium, as shown in Fig. 91. A ΔT heater was soldered to the remaining end of the sample, and the thermocouple on the heater was insulated with mica in order to make a differential connection of thermocouples possible. The differential temperature control system is shown schematically in Fig. 92. The heat-sink control system has been reported in a previous report.¹⁴ The sample holder and thermal shield are placed in the cryostat sample chamber and allowed to rest on the $\frac{1}{8}$ -in. copper plate in the bottom of the chamber. A high vacuum, approximately 3×10^{-7} mm Hg, is pumped on the sample

¹⁴J. C. Pigg, C. C. Robinson, and O. E. Schow, ORNL-2597, p 73-78 (classified).

Fig. 91. Thermoelectric Sample.

chamber and maintained throughout the experiment in order to prevent convection heating of the sample. The sample assembly is shown in Fig. 93.

It should be noted that special effort has been expended in the construction and assembly of the thermocouples, high-vacuum seal, cold junctions, and all wire and switches in the system. When possible, large-diameter (B and S No. 20 gage) thermocouple wire was used. The L & N switch was selected because of its low-thermal-emf characteristics. All solder joints were made with special, low-thermal-emf solder. The cold-junction bath has 32 thermocouples in it and has been designed so that the water is forced to flow from bottom to top over the ice and cold

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Fig. 92. Differential Temperature Control System.

junctions. Such a bath is essential if accurate measurements are to be made.

One interesting feature of the system is that the actual data are measured on the potentiometer. The ΔT control system allows more rapid readings to be made, but the controller does not affect the accuracy of the potentiometer since they are two different and isolated systems.

The major difficulty with the system is that of obtaining the same ΔT at different sample temperatures. Due to the fact that the microvolts-per-degree curve for copper-constantan thermocouples is far from linear, considerable patience is required in adjusting the ΔT controller to the exact ΔT which is desired. The controller will easily hold the required setting; the problem is simply trying to find the proper set point.

The results of the experiment are shown in Figs. 94 and 95.

These data are in good agreement with previously published material on germanium.^{15,16} This agreement indicates that the equipment and procedure are satisfactory.

¹⁵A. E. Middleton and W. W. Scanlon, *Phys. Rev.* 92, 219 (1953).

¹⁶T. H. Geballe and G. W. Hull, *Phys. Rev.* 94, 1134 (1954).

The agreement, however, indicates that curvature at low temperature and the low values at small ΔT are not due to errors introduced by temperature gradients in the atmosphere, as proposed by Middleton and Scanlon. We observe similar effects, but the sample is in a vacuum and is enclosed in a constant-temperature chamber which supplies the cold sink. Although our data agree with those of Geballe and Hull¹⁶ in magnitude and slope for similar samples, we observe a change in thermoelectric power with different values of ΔT , as did Middleton and Scanlon.

ANNEALING OF RADIATION EFFECTS IN GERMANIUM

J. C. Pigg

The investigation reported in the previous report¹⁷ has been continued, with emphasis placed on changes introduced by Co^{60} gamma irradiation. The irradiations were conducted at liquid-nitrogen temperature, and the samples were kept in liquid nitrogen until warmed up for the annealing pulse. After each pulse the sample was returned to liquid-nitrogen temperature. Measurements of

¹⁷J. C. Pigg, *Solid State Ann. Prog. Rep.* Aug. 31, 1958, ORNL-2614, p 9-11.

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Fig. 93. Cryostat Sample Chamber for Thermoelectric Experiment.

Fig. 94. Thermoelectric Power of Unirradiated, *n*-Type Germanium Crystal vs Temperature.

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Fig. 95. Energy Flux per Carrier vs Temperature.

the Hall coefficient and resistivity of the sample were made both at annealing temperature and in liquid nitrogen prior and subsequent to anneal.

Changes in the Hall constant and resistivity of a 15-ohm-cm, *n*-type germanium crystal (EP6-B) are shown in Fig. 96. After a gamma exposure of 2.1×10^{17} photons, the carrier concentration had decreased from 1.596×10^{14} to $1.242 \times 10^{14} \text{ cm}^{-3}$, and the mobility had decreased from 25,580 to $23,320 \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{sec}^{-1}$. The Hall constant shows a curious structure in the region between 3.8 and 4.0 value of $10^3/T$, which may be instrumental. The structure is almost entirely removed by the anneal.

Figure 97 shows the fraction of the irradiation-induced conductivity removed by a series of 15-min pulses. The measurements were made at 77°K after a pulse to the indicated temperature. Approximately 6% of the induced damage is removed by the low-temperature pulse, and no further change is indicated until after the 194° pulse. Above 194°K considerable structure is evident. Since the introduced change was small compared to the initial conductivity, the resolution of the measurement was poor.

Fig. 96. Hall and Resistivity Characteristics of EP6-B as a Function of Gamma Irradiation and Anneal.

Fig. 97. Fractional Anneal of Gamma-Induced Resistivity Changes in EP1-B and EP6-B.

A 30-ohm-cm sample (EP1-B) irradiated in the Co^{60} source to a dosage of 3.64×10^{17} photons resulted in a decrease in carrier concentration from 1.38×10^{13} to $2.69 \times 10^{12} \text{ cm}^{-3}$, and the mobility decreased from 26,950 to 15,820 $\text{cm}^2 \cdot \text{v}^{-1} \cdot \text{sec}^{-1}$. The changes in carrier concentration and mobility in this case were of the same order of magnitude as the initial values. Hence, the observed changes were sufficiently large to yield much greater resolution than in the previous case (Fig. 98). The qualitative shape of the curve agrees with the previous sample, and the structure appears at the same temperature as before. In both cases the fractional change is about 6%. This is in agreement with results obtained at Bell Telephone Laboratories¹⁸ in annealing

of damage introduced by electron bombardment. The annealing of electron-bombarded samples produced no measurable change in the region below room temperature. The change observed here is sufficient for study if Hall and resistivity changes are large enough to yield adequate resolution.

RADIATION EFFECTS ON PLASTICALLY DEFORMED GERMANIUM

J. W. Cleland

J. H. Crawford, Jr.

It has previously been observed¹⁹ that Co^{60} gamma rays produce randomly distributed interstitials and vacancies in germanium. An energy level has been located at $\sim 0.20 \text{ eV}$ below the conduction band by these studies, and this state

¹⁸W. L. Brown, W. M. Augustyniak, and T. R. Waite, *J. Appl. Phys.* 30, 1258 (1959).

¹⁹J. H. Crawford, Jr., and J. W. Cleland, *J. Appl. Phys.* 30, 1204-13 (1959).

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Fig. 98. Hall and Resistivity Characteristics of EP1-B as a Function of Gamma Irradiation and Anneal.

has been ascribed to a mobile interstitial because of its annealing behavior at moderate temperatures. The action of such an interstitial upon anneal is of interest in that the 0.20-eV level apparently disappears; however, the net electron concentration is essentially unchanged. Such a behavior would suggest migration of the interstitial to dislocations or clustering rather than simple annealing.

The dislocation density of germanium can be altered by plastic deformation at elevated temperatures. High-purity, *n*-type single crystals of germanium with an initial dislocation density of $\sim 3000 \text{ cm}^{-2}$, as determined by etch-pit counting, were bent²⁰ at $\sim 800^\circ\text{C}$ to a radius of $\sim 3 \text{ cm}$. This increased the dislocation density to $\sim 10^7 \text{ cm}^{-2}$. Control samples and deformed samples were irradiated with Co^{60} gamma rays. Figure 99, which is a plot of extrinsic carrier concentration vs in-

²⁰We are indebted to Dr. R. A. Logan, of the Bell Telephone Laboratories, for these samples.

Fig. 99. Log Electron Concentration vs Inverse Temperature for Control, Deformed, and Deformed-Annealed Specimens of *n*-Type Germanium Before and Subsequent to Co^{60} Gamma-Ray Irradiations.

verse temperature, indicates that no evidence of the ~ 0.20 -eV energy level was observed for the deformed germanium of high dislocation density, although such a level is apparent in the control sample. The uniform curvature of carrier concentration, as shown in curve A, original; curve B, after 1.40×10^{17} photons; and curve C, after 3.26×10^{17} photons, would suggest a spread of energy levels that already existed in the deformed sample and consequently masked any unique energy level of the type that might be introduced by Co^{60} gamma irradiation.

In addition to those acceptors introduced by dislocations, one must consider vacancies introduced during the deformation and also copper, which has a relatively high diffusivity in germanium. Vacuum anneal at 450°C , however, should effectively remove both vacancies and copper, leaving only those acceptors introduced by the dislocations. A deformed sample, subsequent to such an anneal, is also shown in Fig. 99; and the lack of curvature of the carrier concentration as a function of temperature before exposure indicates that the dislocation acceptor level is a unique value as suggested by Logan²¹ and Read,²² as compared to the spread of energy levels produced by vacancies, copper, and dislocations, as indicated by curve A of Fig. 99.

Cobalt-60 gamma irradiation of a deformed, vacuum-annealed specimen then results in curves of carrier concentration vs temperature that are quite similar to the control curves I, II, and III in the higher temperature region and thus indicate a fairly distinct energy level. It has not yet been possible, however, to observe any large difference upon annealing that could be attributed to preferential migration of interstitial atoms to dislocations.

HALL MOBILITY OF IRRADIATED GERMANIUM

J. W. Cleland

J. H. Crawford, Jr.

The effect of neutron and Co^{60} gamma-ray irradiation on the Hall mobility, μ_H , of *n*-type germanium has been reported in a recent publication.²³ Figure 100 indicates the pronounced

²¹R. A. Logan, G. L. Pearson, and D. A. Kleinman, *J. Appl. Phys.* 30, 885 (1959).

²²W. T. Read, *Phil. Mag.* 45, 775, 1119 (1954).

²³J. H. Crawford, Jr., and J. W. Cleland, *J. Appl. Phys.* 30, 1204-13 (1959); see also abstract, this report.

Fig. 100. *n*-Type Germanium Hall Mobility vs Temperature After Co^{60} Gamma-Ray Irradiations. Curve I — before exposure; curve IV — after 2.3×10^{17} gamma rays/cm²; curve VI — after 5.5×10^{17} gamma rays/cm²; curve VII — after 9.0×10^{17} gamma rays/cm²; curve VIII — after 1.36×10^{18} gamma rays/cm²; curve IX — after 1.73×10^{18} gamma rays/cm²; curve X — after 2.12×10^{18} gamma rays/cm².

variation of charge-center concentration as a function of temperature that is observed for gamma-ray irradiation. This is evident as a knee in the the $\log \mu_H$ vs $\log T$ curve near 160°K. Figure 101 does not indicate any such pronounced variation of charge-center concentration for reactor irradiation, but a general decrease in mobility that extends over the entire temperature range. It has been suggested²³ that this different behavior was primarily due to a different spatial distribution of the damage introduced by the two types of radiation. In order to investigate this point more thoroughly, high-purity, *n*-type samples of germanium were irradiated in Hole 51 of the ORNL Graphite Reactor so that the extrinsic carrier concentration was reduced by an amount comparable to that of Fig. 100. Typical results are shown in Fig. 102, where $\log \mu_H$ is plotted against $\log$ absolute temperature. It is evident

Fig. 101. *n*-Type Germanium Hall Mobility vs Temperature After Fast-Neutron Irradiations. Curve I — before exposure; curve IV — after 4.32×10^{15} neutrons/cm²; curve VII — after 1.01×10^{16} neutrons/cm²; curve IX — after 1.10×10^{16} neutrons/cm².

from these curves that neutron bombardment reduces the absolute value of the slope for temperatures below 220°K and causes a decrease in magnitude of μ_H but little change in slope above that temperature.

It is possible to understand this behavior on the basis of the disordered-region model for fast-neutron damage with the following refinement: As has been shown,^{23,24} the disordered region resulting from a single fast-neutron collision is surrounded by a space-charge zone of considerably greater spatial extent ($\sim$ an order of magnitude) than the disordered region itself. Most of this space-charge zone, which contains a potential gradient, is capable of blocking current flow in an otherwise slightly damaged matrix. The radius of the space-charge zone effective for blocking current flow is temperature dependent, being larger the lower the temperature. The temperature dependence has two sources: (1) the

²⁴B. R. Gossick, *J. Appl. Phys.* 30, 1214-18 (1959).

Fig. 102. *n*-Type Germanium Hall Mobility vs. Temperature After Fast-Neutron Irradiations. Curve I - before exposure; curve II - after 1.44×10^{14} neutrons/cm²; curve III - after 1.44×10^{14} (more) neutrons/cm²; curve IV - after 9.6×10^{13} (more) neutrons/cm²; curve V - after 4.8×10^{13} (more) neutrons/cm².

variation of the total potential difference, ψ_p , between the disordered region and the matrix:

$$\psi_p = \frac{1}{q} \left(E_g - kT \ln \frac{AT^3}{N_1 N_2} \right),$$

where q is the electronic charge, E_g is the band gap, A is a constant, and N_1 and N_2 are the net acceptor concentration in the disordered region and the net donor concentration in the matrix, respectively, and (2) the range into the space-charge zone that conduction electrons can penetrate. The latter effect depends on electron energy and, hence, kT . Therefore, it appears that most of the apparent change in μ_H and its temperature dependence is due to a change in the effective cross section of the specimen for carrying current and does not reflect a change in the mobility of the matrix itself. A quantitative theory to account for this effect is being developed.

THE DIFFUSION OF COPPER IN GERMANIUM

J. W. Cleland

J. H. Crawford, Jr.

The diffusivity, solid solubility, and acceptor behavior of certain "deep-level" impurities in germanium has been extensively investigated.²⁵ Introduction of copper to germanium by diffusion at an elevated temperature, followed by rapid quenching to avoid annealing, results in a super-saturated solution with acceptor states located 0.26 eV below the conduction band and 0.33 and 0.04 eV above the valence band.

High-purity, single-crystal Hall plates of *n*-type germanium, with an original electron concentration of 4.6×10^{15} cm⁻³ at 77°K, were electroplated with a visible layer of copper and then heated in an atmosphere of helium for 20 hr at 650°C. The samples were quenched by placing them on a large metal block immediately upon removal. The electron concentration was then determined as $\sim 1.0 \times 10^{15}$ cm⁻³ at 77°K for several specimens. Thus, 3.6×10^{15} electrons/cm³ were removed by the introduction of copper and, possibly, vacancies that were quenched in simultaneously. Published literature²⁶ lists the solid solubility at this copper-germanium eutectic temperature as 1.0×10^{15} cm⁻³. If copper is a triple acceptor, then 3.0×10^{15} electrons/cm³ would be removed by this experiment.

R. A. Logan²⁷ has examined the effect of dislocation density on subsequent annealing of copper in germanium. Material containing $\sim 10^6$ dislocations/cm², as determined by etch-pit counts, totally annealed (precipitation of copper) in 1 hr at 500°C, whereas material of relatively low dislocation density, $\sim 10^4$ cm⁻², required 24 hr at 500°C. The final copper concentration is thus dependent upon the number of nucleation sites and the rapidity of quenching for material of high dislocation density.

The effect of annealing at various temperatures on the electron concentration of a typical sample is shown in Fig. 103, where log Hall coefficient and resistivity are plotted vs inverse temperature for various treatments. Curves I represent the original sample; and curves II were taken after

²⁵W. W. Tyler, *Phys. and Chem. Solids* 8, 59 (1959) and references contained therein.

²⁶H. H. Woodbury and W. W. Tyler, *Phys. Rev.* 105, 84 (1957).

²⁷R. A. Logan, *Phys. Rev.* 100, 615 (1955).

Fig. 103. Log Hall Coefficient and Resistivity vs Inverse Temperature for *n*-Type Germanium After Copper Diffusion, Annealing, and Radiation Experiments.

diffusion at 650°C, rapid quenching, and a subsequent anneal of 40 hr at 450°C in vacuum. Curves III were obtained after 60 hr at 500°C in vacuum, and curves IV are after 20 hr at 590–600°C in vacuum. The final carrier concentration after the above is 1.5×10^{15} electrons/cm³ at 77°K. Thus, 3.1×10^{15} electrons/cm³ are still trapped, presumably by $\sim 1 \times 10^{15}$ copper atoms/cm³. It is instructive that the final carrier concentration agrees so closely with the expected carrier concentration, using the published solubility of copper in germanium at 650°C. It is possible that the relatively small increase in electron concentration as a result of the various anneals is primarily due to removal of vacancies that were introduced in the initial quench and that this sample actually indicates virtually no precipitation of copper to nucleation sites. The dislocation density of the samples employed is not known, but it will be ascertained by the technique of etch-pit counting.

Curves V of Fig. 103 were obtained after an exposure to $\sim 2.4 \times 10^{14}$ fast neutrons in Hole 51

of the ORNL Graphite Reactor. The sample was shielded in boral to minimize thermal-neutron absorptions. The final carrier concentration after exposure was 7.5×10^{14} electrons/cm³; thus, 7.5×10^{14} electrons were removed by the irradiation. These values are in excellent agreement with the published removal rate²⁸ of ~ 3.2 electrons per incident fast neutron for this particular position in the Graphite Reactor. The end result, therefore, is the formation of $\sim 3.75 \times 10^{14}$ interstitial-vacancy pairs under the most simple assumption that radiation produces Frenkel defects. These might be expected to serve as nucleation sites; however, curves VI, after an anneal of 16 hr at 450°C in vacuum, were identical with curves IV, which were obtained before the irradiation. Thus, the radiation-produced defects were completely removed without any apparent effect on the previously introduced copper acceptor states.

EFFECT OF NEUTRON SPECTRUM ON CONDUCTIVITY CHANGE IN GERMANIUM

D. Binder

It has been observed in the ORNL Graphite Reactor that Hole 51N is 2.0 ± 0.4 times as effective as Hole C for conductivity changes in *n*-type germanium.²⁹ On the other hand, the neutron flux greater than 0.6 Mev is at least five times greater for Hole 51N than for Hole C.³⁰ Since Hole 51N contains a uranium converter and Hole C is well moderated, the flux spectrum in 51N has a higher average energy above 0.6 Mev. It follows that, if the high-energy flux were dominant in the germanium effect, the ratio for the conductivity change in Hole 51N relative to Hole C would be at least 5 instead of 2. This indicates that the neutron flux less than 0.6 Mev is highly effective in Hole C.

To fit the ratio of 2, an approximate analysis shows that it is necessary to assume a saturation of the germanium effect with neutron energy. Assuming a $1/E$ spectrum below 0.6 Mev for Hole C, it is found that the saturation occurs in the region of 0.2-Mev neutrons. The analysis is based on the assumption of ionization loss as the

²⁸J. H. Crawford, Jr., and J. W. Cleland, p 67–107 in *Progress in Semiconductors*, vol 2, Heywood and Co., LTD., 1957.

²⁹J. W. Cleland, private communication.

³⁰D. Binder, *Solid State Ann. Prog. Rep. Aug. 31, 1958*, ORNL-2614, p 114.

limiting process. A neutron of energy E produces recoils of energy zero to $E/18$. The recoils are assumed to ionize only above a critical energy $E_c/18$. The best fit of the data occurs at about a neutron energy E_c of 0.2 Mev.

Ionization losses are only one possible cause for the saturation. Defect aggregates may produce zones³¹ that are less effective than the same number of isolated point defects. Since the number of defects is linear with neutron energy, the aggregates cause a saturation of the effect with neutron energy. Assuming that aggregates are more probable at higher energies, and point defects at the lower energies, then the neutron energy for which the two are competitive is about 0.2 Mev.

GAMMA IRRADIATION OF n -TYPE SILICON

L. C. Templeton E. Sonder

During the last year it has become more apparent than ever that the energy-level structure produced by irradiation of semiconductors is not by any means simple. Different irradiation particles seem to affect materials differently.³² Different investigators at times seem to obtain seemingly contradictory results. History and impurities in samples seem to have an effect.³³ Thus, the careful and systematic investigation of the energy-level structure produced by Co^{60} gamma rays in the upper half of the energy gap of silicon (which we started last year³⁴) seems more than ever called for. We will present here Hall effect data on three additional samples, all grown by the same producer in quartz crucibles.³⁵ A few tentative conclusions will be drawn from a comparison of the introduction rate of traps and the Fermi level of the various samples. It is planned in the future to

compare these results with similar ones on silicon grown by the floating-zone technique in order to verify or contradict the theory³³ that the trap level usually seen in irradiated, n -type silicon requires the presence of oxygen.

The Hall coefficients for samples having had a preirradiation net donor density of 9×10^{13} (1123-3), 1.5×10^{14} (1123-4), and 2.1×10^{15} (1019-2) and having been irradiated at room temperature with various amounts of Co^{60} gamma rays are shown as a function of reciprocal temperature in Figs. 104–106. All the samples shown indicate that a single trapping level is present, which traps out donor electrons in the range 100–250°K. However, even though the trapping level seems to be the same in all samples, its introduction rate is different for various samples, as shown by the different slopes in Fig. 107. In that graph is shown the number of net acceptors, including compensating boron atoms originally in the material (this had been determined by the

Fig. 104. Hall Coefficient of Sample 1123-3 Plotted vs Inverse Temperature.

³¹J. H. Crawford, Jr., and J. W. Cleland, *J. Appl. Phys.* 30, 1204–13 (1959).

³²For a review of the field see *J. Appl. Phys.* 30(8) (1959).

³³G. D. Watkins, J. W. Corbett, and R. M. Walker, *J. Appl. Phys.* 30, 1198 (1959).

³⁴E. Sonder and L. C. Templeton, *Solid State Ann. Prog. Rep. Aug. 31, 1958*, ORNL-2614, p 20.

³⁵The samples were grown by Silicon Crystals, Inc., Wilmington, Del. It has been shown that silicon grown from quartz crucibles may contain 10^{18} oxygen atoms/cm³ [Lederhandler and Patel, *Phys. Rev.* 108, 239 (1957) and references given therein].

Fig. 105. Hall Coefficient of Sample 1123-4 Plotted vs Inverse Temperature.

manufacturer from segregation coefficients and growth data) vs total number of irradiating photons. The two less-pure samples have introduction rates between 1 and 1.1×10^{-3} trap/cm³ per photon/cm², while for the purer samples the introduction rate is about two-thirds that amount, or $0.67-0.69 \times 10^{-3}$. It is also evident from Fig. 107 that, within experimental error, the introduction rates (slopes) of the four samples seem to be independent of the total amount of irradiation; that is, the trap density seems to be proportional to the total integrated gamma flux.

In order to be able to discuss these results, it is very useful to determine how the Fermi level varies with irradiation and temperature. This can be done, for the number of electrons, n , in the conduction band, which determines the Hall coefficient, is given by the equation

$$n = N_c \exp \left(-\frac{E_c - \zeta}{kT} \right),$$

where $E_c - \zeta$ is the energy difference between the conduction band edge and the Fermi level and where N_c , the density of states in the conduction band, is given by $N_c = 2\omega(2\pi m^* kT/h^2)^{3/2}$; m^* is

Fig. 106. Hall Coefficient of Sample 1019-2 Plotted vs Inverse Temperature.

the density-of-states effective mass; ω is the number of energy minima, which for silicon is 6; k is the Boltzmann constant; and T is the absolute temperature. Figure 108 shows the Fermi level as a function of temperature for specimen 1123-4 calculated in that way. The two curves shown are for the unirradiated sample and for the sample irradiated until there were about $\frac{5}{6}$ as many traps as there were donor centers. Results for specimens 1123-2 and 1123-3 are not shown since, except for differences in position and slope

Fig. 107. Total Number of Acceptor Centers as a Function of Integrated Gamma Flux.

Fig. 108. Variation of the Fermi Level with Temperature for Specimen 1123-4 Before and After Gamma Irradiation.

of the curves, they are quite similar in form. However, in the case of specimen 1019-2, where irradiation was continued until there were about $1\frac{1}{2}$ times as many traps as there were donors, a definite pinning of the Fermi level can be observed in Fig. 109. From the position of the pinned Fermi level the energy of the trap level can be obtained. From the Hall data in Fig. 106 it can be seen that, in the case of the heaviest irradiation, less than 2% of the electrons remain in the conduction band below 150°K. Also, since the donor levels are more than 0.1 eV above the Fermi level, they are empty. Thus, essentially all the electrons are in the traps, so that the left side of the equation

$$\frac{n}{N_{\gamma}} = \left(1 + \exp \frac{E_{\gamma} - \zeta}{kT} \right)^{-1}$$

is equal to the number of donor electrons available divided by the number of introduced traps, or $\frac{2}{3}$. The position of the trap level calculated in that way is 0.175 eV below the conduction band, which is somewhat deeper than the 0.16 that had been reported by Wertheim.³⁶

It should be pointed out that there is one uncertainty that is always present when Hall-effect measurements are used to determine energy levels.

³⁶G. K. Wertheim, *Phys. Rev.* 110, 1272 (1958).

Fig. 109. Variation of Fermi Level with Temperature for Specimen 1019-2.

This comes from the uncertainty in the mobility ratio that enters the Hall-effect expression. The maximum uncertainty in it is a factor of 2, making the Fermi-level calculation inaccurate by at most the amount $kT \ln 2$, which for the determination of the trapping level is at most 0.007 ev.

We shall now try to see if the change in introduction rate is related to the position of the Fermi level. We shall think in terms of two possible processes. In one case identical damage (at the same rate) is introduced in all the samples. However, due to different positions of the Fermi level at the temperature at which measurements are made, some of the trapping levels which are active in two of the specimens will be inactive as traps in the others. In the other case it is assumed that, due to differences in impurity concentration or the Fermi level at the irradiation temperatures, different processes for reorientation of the irradiation-produced imperfections may take place. This might then cause different damage rates to be observed. In Table 18 are listed the four specimens with their original donor and acceptor concentrations, the introduction rates of the traps observed, and the Fermi levels calculated, both for the temperature of irradiation and for the temperature at which the density of traps is observed (111°K). It should be evident even from the graphs of Figs. 108 and 109 that the

irradiation-temperature Fermi level is not changed appreciably by the irradiation (but it is different in the different samples) but that the 111° Fermi level changes quite appreciably each time the specimens are irradiated. Now if the first process described above were the one causing the observed introduction rate change, then the 111° Fermi level could be expected to be in one range for the two samples with the slow introduction rate and in another range for the samples with the faster rate of introduction. The data, however, show that the Fermi level in all the samples covers approximately the same range of values. This leads us to believe that the second process is the more likely, that is, that the 0.17-ev level seen is actually introduced at different rates in the two sets of samples, due either directly to differences in the impurity concentration of the samples or to differences in Fermi level, which may cause the irradiation-induced imperfections to have different charge states in different samples.

In connection with the above-reported Hall-effect measurements, the Hall mobility has been determined as a function of temperature for the various irradiations. In most of the samples a moderate decrease in the mobility is observed below about 150°K. As the temperature is lowered further, the mobility decreases more, as one would expect for charged-impurity scattering. However, in the case

Table 18. Comparison of Introduction Rates and Fermi Levels

	Specimen			
	1123-3	1123-4	1123-2	1019-2
Resistivity (300°K), ohm-cm	53	30	12.0	2.1
N_d = donor density, cm^{-3}	1×10^{14}	2×10^{14}	5×10^{14}	2.5×10^{15}
N_a = acceptor density, cm^{-3}	4×10^{13}	5×10^{13}	1×10^{14}	3×10^{14}
Introduction rate of traps, $\text{traps} \cdot \text{cm}^{-1} \cdot \text{photon}^{-1}$	0.67×10^{-3}	0.69×10^{-3}	1.00×10^{-3}	1.06×10^{-3}
Fermi level at irradiation temperature (320°K), ev	0.355	0.343	0.316	0.265
Fermi level at 111°K				
Before irradiation	0.106	0.102	0.105	0.076
After first irradiation	0.110	0.105	0.108	0.082
After second irradiation	0.129	0.109	0.119	0.091
After third irradiation	0.136	0.119	0.127	0.113
After fourth irradiation				0.166

of the purest sample (1123-3) a very precipitous drop in the mobility was observed. The results are shown in Fig. 110. Obviously, the slope in the temperature range 60–130°K, for the sample irradiated with 1.31×10^{17} photons/cm², is much greater than the $\frac{3}{2}$ power one would expect for charged-impurity scattering. It is a bit surprising that most of the rapid mobility change occurs below 110°, where, according to the Hall data in

Fig. 110. Hall Mobility of Sample 1123-3 as a Function of Temperature and Irradiation.

Fig. 104, there is little change in the number of conduction electrons and presumably, also, the electrons on donors and traps. These mobility results have yet to be explained.

MAGNETISM OF INTERACTING DONORS

E. Sonder

H. C. Schweinler

Introduction

The magnetic behavior of semiconductors at low temperature is very strongly dependent upon the degree of doping. In highly doped material, after merging of the conduction band and impurity levels has occurred, the magnetism of the impurity centers is completely overwhelmed by the band magnetism of the merged band. This has been observed in heavily doped germanium,³⁷ where for donor densities greater than 10^{18} cm^{-3} the conduction band diamagnetism sufficed to explain the data. The other extreme case, that of such low doping density that the overlap between donor centers was negligible, has also been observed, in this case in silicon³⁸ with less than 2×10^{17} donors/cm³. Here the contribution of the conduction band is absent below 50°K because all of the conduction electrons are frozen out on donor centers. The magnetism of these latter is well-represented by a Curie law and is proportional to the number of donors. Both of these extreme situations are reasonably simple, and agreement between theory and experiment seems to obtain. However, when the amount of doping is between these extremes, a more complicated behavior is observed. We shall be concerned here with the magnetic behavior when the doping becomes somewhat greater than in the simple isolated donor extreme case. The experimental facts, which have clearly been observed in the case of silicon,³⁸ are that the slope of the Curie curve of susceptibility vs inverse temperature decreases as the temperature is lowered and that, even at higher temperatures, as the donor density is increased above about $2 \times 10^{17} \text{ cm}^{-3}$, the slope deviates more and more from that expected for independent donor centers. In germanium there seems to be an indication of a similar behavior;³⁷ however, it occurs in appreciably purer samples ($5 \times 10^{16} \text{ cm}^{-3}$). Because of limitations on the sensitivity

³⁷R. Bowers, *Phys. Rev.* 108, 683 (1957).

³⁸E. Sonder and D. K. Stevens, *Phys. Rev.* 110, 1027 (1958).

of the measurements, no systematic data on impurity contribution have been obtained for germanium.

Theoretically, there are two obvious approaches to the treatment of this intermediate situation. One is to start from ideas related to impurity banding and to apply these to the magnetic properties. Such a calculation has been made by Mooser.³⁹ There seem to be two problems in this type of approach. The first is that a band resulting from a "random lattice" has not yet been satisfactorily treated in a theoretical sense and that, therefore, the impurity band is usually approximated by one for a direct lattice of appropriately large lattice spacing. The second is that the one-electron picture neglects the electrostatic repulsion between electrons, which becomes appreciable as the band gets narrower, becoming so great in the limit of weakly overlapping atomic orbitals as to reduce effectively the number of states in the band by a factor of 2. (A completely banded donor band has states for $2N_d$ electrons, while for the separated donors there are available one-electron states for only N_d electrons.) The other approach to the treatment of weakly interacting donors, which is the one we shall use, starts from the independent donors and permits weak interactions of only two at a time. This approach was suggested independently by Hedgcock⁴⁰ and by Sonder and Stevens³⁸ to explain the experimental results for germanium and silicon, respectively. Hedgcock has made an estimate of the effect by dividing the donors into two groups, those which are independent and therefore magnetically active and those which are paired as diatomic molecules and are consequently nonmagnetic. He has used the hydrogen molecule equilibrium distance, corrected, of course, for the dielectric constant of the semiconductor and the effective mass of the donor electrons, as the distance which determines whether a given pair of donors is to be considered a molecule or a pair of independent atoms. The correct order of magnitude for the effect was obtained from this simple model, making it seem worth while to calculate the consequences of interactions of donors in pairs more carefully,

taking into consideration the variation of electron binding energy with distance between donors as well as the change with temperature in the ratio of bound to unbound pairs of electrons.

The Hydrogenic Model for the Donor Center

The problem of equilibrium energy levels of a particle in an inverse square force field (the hydrogen atom) has been solved exactly both semiclassically⁴¹ and quantum mechanically.⁴² Using these solutions, it is quite simple to compare the expressions for the energy levels, as well as the mean radii of the wave functions (Bohr orbits in the semiclassical treatment) for particles of unit electronic charge but different masses moving in media with different dielectric constants. The following expressions result:

$$\frac{E_1}{E_2} = \frac{m_1/K_1^2}{m_2/K_2^2} \quad (1a)$$

and

$$\frac{\bar{r}_1}{\bar{r}_2} = \frac{K_1/m_1}{K_2/m_2}, \quad (1b)$$

where the subscripts 1 and 2 refer to two particles, respectively, of mass m_1 and m_2 in media of dielectric constant K_1 and K_2 ; $\bar{r}$ refers to the mean radius; and E refers to the energy of a given state of the system. In the hydrogenic model of the donor center in a semiconductor, this type of comparison is made between the donor (electron mass, m^* , in a medium of dielectric constant, K) and the hydrogen atom (electron mass, m_e in vacuum). The assumptions that are implicit in this derivation should be kept in mind, however. A semiconductor is not really a continuous medium; neither is the concept of a dielectric constant perfectly valid in a region containing only a few hundred atoms. If these assumptions are accepted, however, then the model can be used to treat the interactions of two centers. Solutions for the

³⁹E. Mooser, *Phys. Rev.* 100, 1589 (1955).

⁴⁰F. T. Hedgcock, *Can. J. Phys.* 37, 381 (1959).

⁴¹See, for instance, G. Herzberg, *Atomic Spectra and Atomic Structure*, p 15 ff., Dover Publications, New York, 1944.

⁴²See, for instance, L. I. Schiff, *Quantum Mechanics*, p 80 ff., McGraw-Hill, New York, 1949.

energies and separation distances of the lowest-lying eigenstates of a hydrogen molecule or molecule ion have been calculated⁴³⁻⁴⁷ or deduced from spectroscopic data.⁴⁸ These, in conjunction with Eqs. (1), will yield the energies of the magnetic and nonmagnetic states of donor pairs as a function of their separation distance. This information will then make it possible to obtain the magnetic susceptibility as a function of donor density and temperature.

The Magnetic Susceptibility of Two-Donor Molecules

The magnetization, M (magnetic moment per unit volume), may be defined in terms of the partition sum, Z , of a system by the expression

$$M = kT \frac{d \ln Z}{dH}, \quad (2)$$

where H is the magnetic field strength, k is the Boltzmann constant, and T is the absolute temperature. The system which we shall consider will consist of unit volume of the crystal containing $N_d/2$ two-donor systems, in which we shall assume that all electrons are frozen out of the conduction band. The grand partition sum in the presence of a magnetic field will then contain only terms for zero-, one-, and two-electron states of the two-donor centers, giving

$$Z = \prod_{i=1}^{N_d/2} Z_i = \prod_{i=1}^{N_d/2} \left[e^0 + \sum_j e^{\eta - \epsilon_j} (e^{\beta H/kT} + e^{-\beta H/kT}) + \sum_k e^{2\eta - \epsilon_k} (e^{2\beta H/kT} + 1 + e^{-2\beta H/kT}) + \sum_{k'} e^{2\eta - \epsilon_{k'}} \right]. \quad (3)$$

Here ϵ and η are the energy of a given eigenstate and the Fermi energy, respectively, both in units

⁴³ E. Teller, *Z. Physik* 61, 458 (1930).

⁴⁴ H. M. James and A. S. Coolidge, *J. Chem. Phys.* 1, 825 (1933).

⁴⁵ H. M. James, A. S. Coolidge, and R. D. Present, *J. Chem. Phys.* 4, 187 (1936).

⁴⁶ J. C. Slater, "Electronic Structure of Atoms and Molecules," Tech. Report No. 3, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, 1953.

⁴⁷ O. W. Richardson, *Proc. Roy. Soc. (London)* 152, 503 (1935); *Molecular Hydrogen and Its Spectrum*, Yale University Press, New Haven, 1934.

of kT , and β is the Bohr magneton. The sum over j refers to a sum over all one-electron states of a single two-donor center, while the sums over k and k' refer to sums over triplet and singlet two-electron states of one molecule, respectively. The two lowest one-electron molecule ion orbitals ($1s\sigma$ and $2p\sigma$) suffice to describe atom and bare donor, and the lowest singlet and triplet two-electron states ($^1\Sigma_g$ and $^3\Sigma_u$) suffice to describe all neutral atoms in the ground states. All other excited states are much higher in energy⁴⁹ for the conditions which we are considering. Our two-donor grand partition function can thus be approximated by a sum of five terms.

It should be pointed out here that the terms Z_i within the product in Eq. (3) are not all the same since the electronic energies $E = kT\epsilon$ differ for different separation distances of the molecules. However, the partial potential of the electrons (Fermi energy) $\mu = kT\eta$ is a constant throughout the whole sample and is determined by the number of electrons present, which is, of course, equal to the donor concentration N_d . The relation between this number and the Fermi energy is given by

$$N_d = kT \frac{d \ln Z}{d\mu} = \frac{d \ln Z}{d\eta}. \quad (4)$$

Performing the differentiation indicated in Eqs. (2) and (4) and expanding terms of the form $\exp(\beta H/kT)$ to first order in $\beta H/kT$ yields for N_d

⁴⁸ R. Rydberg, Dissertation, Stockholm, 1934, unpublished; reproduced in Herzberg, *Molecular Spectra and Molecular Structure. I. Diatomic Molecules*, Prentice-Hall, New York, 1939.

⁴⁹ The lowest excited singlet two-electron state, for instance, is the $^1\Sigma_u$, which in hydrogen is more than 11 eV above the ground state. (See diagram in Herzberg, ref 48, p 340.) This would correspond to about 0.03 to 0.04 eV in silicon or a temperature above room temperature.

and M the following expressions:⁵⁰

$$N_d = \sum_i (N_d)_i = \sum_i \frac{2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 6e^{2\eta-\epsilon_3} + 2e^{2\eta-\epsilon_1}}{1 + 2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 3e^{2\eta-\epsilon_3} + e^{2\eta-\epsilon_1}} \quad (5)$$

and

$$M = \frac{\beta^2 H}{kT} \sum_i \frac{2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 8e^{2\eta-\epsilon_3}}{1 + 2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 3e^{2\eta-\epsilon_3} + e^{2\eta-\epsilon_1}} \quad (6)$$

where ϵ_s and ϵ_p are the energies of the one-electron states and ϵ_1 and ϵ_3 are the energies of the singlet and triplet two-electron states, respectively, all in units of kT . If it is noted that the denominators in Eqs. (5) and (6) are identical, these expressions can be combined as follows:

$$M = \frac{\beta^2 H}{kT} \sum_i \left[(N_d)_i - \frac{2(e^{2\eta-\epsilon_1} - e^{2\eta-\epsilon_3})}{1 + 2(e^{\eta-\epsilon_s} + e^{\eta-\epsilon_p}) + 3e^{2\eta-\epsilon_3} + e^{2\eta-\epsilon_1}} \right] \quad (7)$$

Equation (7) can be simplified by defining the energy difference $\epsilon_{31} = \epsilon_3 - \epsilon_1$ and assuming that the compensation, if it exists at all, is not of very great magnitude (e.g., is less than 25%), permitting the neglect of zero- and one-electron states.⁵¹ The resultant expression for the magnetic moment is

$$M = \frac{\beta^2 H}{kT} \sum_{i=1}^{N_d/2} \left[(N_d)_i - \frac{2(1 - e^{-\epsilon_{31}})}{1 + 3e^{-\epsilon_{31}}} \right] \quad (8)$$

The first term in this sum is, of course, simply the total number of electrons.

Distribution of Separation Distances for Two-Donor Systems

The sum in Eq. (8) may be converted to an integral, since $N_d/2$ is a very large number. However, it must be recalled that the triplet-singlet splitting energy, ϵ_{31} , may be a strong

function of the donor-pair separation so that, if our integral is to be over the separation distance, r , a weighting function, or probability of finding a donor pair with a given separation distance, must be determined. This we shall now do.

If the donors are distributed at random, then we can fasten our attention on one donor and determine the probability that there is no nearest neighbor closer than r and also one neighbor in the spherical shell volume element $4\pi r^2 \Delta r$ at r . This will give the probability of finding a nearest neighbor in Δr at r . We use the Poisson distribution, which gives the probability $P(N)$ of exactly N events in terms of the expectation value, G :

$$P(N) = \frac{G^N}{N!} e^{-G}$$

The expected number of donors in a volume V is $N_d V$, where N_d is the donor density. This gives for the probability of no neighbors closer than radius r ,

$$P(0,0;r) = \exp\left(-\frac{4\pi}{3} N_d r^3\right)$$

⁵⁰The assumption $\beta H \ll kT$ is good above 3°K, since for the magnetic fields usually used in susceptibility measurements $H \lesssim 20$ kilosterds or $\beta H/k \lesssim 0.4$.

⁵¹In n -type silicon, for instance, at temperatures in the neighborhood of 10°K the Fermi level is ~ 0.025 ev below the conduction band edge, while the energies of the one- and two-electron states of a pair of donors of intermediate separation are -0.06 and -0.10 ev, respectively. The exponents $\mu - \epsilon_s$ and $2\mu - \epsilon_1$ at this temperature are accordingly 41 and 58, respectively.

and for the probability of finding one neighbor in a shell of thickness Δr at r ,

$$P(1, r: r + \Delta r) = N_d 4\pi r^2 \Delta r \exp(-N_d 4\pi r^2 \Delta r) .$$

The product of these two probabilities will yield the expression applicable for our case, which for infinitesimal Δr is given by

$$dP = 4\pi N_d r^2 dr \exp\left(-\frac{4}{3}\pi N_d r^3\right) . \quad (9)$$

The relative probability dP/dr of finding the nearest neighbor at r is graphed in Fig. 111.

Fig. 111. Relative Probability, dP/dr , of Finding the Nearest Neighbor of a Given Donor at a Distance r from It.

The remainder of this section will be devoted to a discussion of the validity of the assumptions made concerning the above distribution function; the reader may wish to go directly to the following section, where an approximate expression for the magnetic moment is obtained.

Equation (9) is strictly correct only for the donors which make up the first pair. It would be correct for all pairs if already-paired donors were still available for further pairing. This is obviously not the case. However, let us point out that we are here interested in the situation where only a fairly small fraction of donors are close enough to be considered effectively paired (i.e., such that some of the magnetism is removed). The fraction of groups of three in such cases will

be even smaller. Moreover, if we pick our pairs in such a way as to remove from consideration first the pairs of closest spacing, then by the time deviations between Eq. (9) and the actual distribution of distances becomes significant, we will be dealing with pairs that have such large separation that their contribution to the magnetic moment is exactly what it would be if the donors were unpaired and is thus independent of the separation distance.

In order to make a more quantitative estimate of the error resulting from use of Eq. (9), we can define a separation distance beyond which pairs will act like independent donors by such a criterion as $E_{31} = 2kT$. Then let all the $N_d(N_d - 1)/2$ inter-donor distances be listed in order of increasing magnitude, and use them in this order to fill in the low-separation tail of the distribution given by Eq. (9). Eventually one of the members of the pair currently being chosen will be found to have been paired with another donor previously. An estimate of the possibility for this event is given by the probability that the neighbor at distance r is a *next* nearest neighbor, that is, that there exists *one* atom within the sphere of radius r and, also, one in the vicinity of the surface. This probability is given by

$$dP' = \frac{4}{3}\pi N_d r^3 4\pi N_d r^2 dr \exp\left(-\frac{4}{3}\pi N_d r^3\right) . \quad (10)$$

The over-all probability for this event should be doubled because either of the atoms of the pair we are currently picking might have been chosen previously; the probability that both have been selected previously is neglected. Summing over all of the pairs as we pick them, starting from the first, will give an estimate of the total number which have been discarded due to prior pairing. This total number discarded is given by

$$D = 2 \int dP' \\ = 2 \int_0^V N_d V \exp(-N_d V) N_d dV , \quad (11)$$

where $V = (4/3)\pi r^3$ is the volume. For small V , which is now the range of interest, $D \approx (N_d V)^2$. Comparing this with the total number of pairs which have already been picked,

$$\# = \int dP = \int_0^V \exp(-N_d V) N_d dV \approx N_d V , \quad (12)$$

we find for the ratio $D/\# = N_d V$. This shows that the relative number of discards to the number of pairs picked is, for $V < 1/N_d$, $\approx N_d V$ or $N_d (4/3)\pi r^3$. Therefore, if the criterion $E_{31} = 2kT$ is satisfied when r is approximately $\frac{1}{3}$ of the maximum of the distribution given by Eq. (9), as is the case here, then the error resulting from the use of Eq. (9) will be only a few per cent.

It might be pointed out from the foregoing discussion that, when r approaches $r_{\max}$ too closely, the number of rejects becomes appreciable and the present calculation may overestimate the effect of pairing by a factor of 2. This is also evident from a qualitative consideration of the pairing process.

The assumption of a statistically random distribution of donor centers is, strictly speaking, not exact because there is an energy of interaction between every pair of donors. This energy rises sharply for small internuclear distances for the same reason that the hydrogen molecule and hydrogen molecule ion have high energies in the corresponding case of small internuclear distances. If the energy of electrostatic interaction e^2/Kr of the two donor ions⁵² be equated to a multiple of kT_m , say $2kT_m$, and the volume corresponding to this radius be excluded from consideration, the effect on the final results is slight (less than 1%) for the conditions of validity of this theoretical analysis. Such an effect will be neglected in the following.

Evaluation of the Magnetic Moment

From Eq. (8) we get for the magnetic moment of the crystal, using Eq. (9) and the appropriate normalization to a total of $N_d/2$ two-donor systems,

$$M = \frac{\beta^2 H}{kT} \int \frac{N_d}{2} \left\{ 2 - \frac{2[1 - \exp(-\epsilon_{31})]}{1 + 3 \exp(-\epsilon_{31})} \right\} \exp(-VN_d) N_d dV, \quad (13)$$

where $V = (4/3)\pi r^3$. If it is recalled that the magnetic moment for isolated donors is $\beta^2 H N_d / kT$, then it is evident that the value given by Eq. (13) is that for isolated donors multiplied by the correction factor $(1 - I)$, where

$$I = \int \frac{1 - \exp(-\epsilon_{31})}{1 + 3 \exp(-\epsilon_{31})} \exp(-N_d V) N_d dV. \quad (14)$$

This latter expression, of course, has the correct asymptotic behavior, vanishing for small ϵ_{31} and causing the paramagnetism to disappear for large ϵ_{31} .

In order to evaluate the correction I , it is necessary to know how E_{31} varies with separation distance. This can be obtained from calculations on the hydrogen molecule. Figure 112 shows the variation with internuclear distance of the energies of the singlet and triplet states of a hydrogen molecule, as well as the difference $E_3 - E_1 = (E_{31})_H$. The points shown on the difference curve of Fig. 112 are obtained from the calculated values of E_3 and E_1 shown, while the dashed curve shows the approximation to be used later,⁵³ $(E_{31})_H = A_H \exp(-B_H V)$, where $A_H = 9.66$ ev and $B_H = 7.84 \times 10^{22} \text{ cm}^{-3}$. The hydrogenic expression must be scaled for dielectric constant and effective mass, giving

$$E_{31} = \frac{m^*}{K^2} (E_{31})_H = \frac{m^*}{K^2} A_H \exp \left[-B_H \left(\frac{m^*}{K} \right)^3 V \right],$$

where the effective mass, m^* , and dielectric constant K have been left in the equation explicitly as parameters. In Fig. 113 is shown the function

$$f(\epsilon) = \frac{1 - \exp(-\epsilon)}{1 + 3 \exp(-\epsilon)}.$$

As can be seen from the figure, the broken line is a reasonably good approximation ($\sim 10\%$), and it

will be used in the integration of Eq. (14). [The explicit form is $f(\epsilon) = \epsilon/3.7$ for $0 < \epsilon < 3.7$ and $f(\epsilon) = 1$ for $\epsilon > 3.7$.] These approximations lead

⁵²Actually, the ions are screened by the conduction electrons with a Debye length of $\lambda_D = (4\pi N_d e^2 / KkT)^{-1/2}$. However, near the melting point $\lambda_D \approx 100 \text{ \AA}$, which is much larger than the pertinent distances here ($\sim 5 \text{ \AA}$).

⁵³A Heitler-London calculation (see, e.g., Pauling and Wilson, *Introduction to Quantum Mechanics*, p 340 ff., McGraw-Hill, New York, 1935) gives for the splitting $E_{31} = f(r) \exp(-2r)$, where $f(r)$ is a moderately complicated function. However, as Fig. 112 shows, the fit of $A \exp(-BV)$ is quite satisfactory in the range of greatest importance. The use of this latter function makes it possible to perform certain integrations which occur later.

Fig. 112. Energies of the Singlet and Triplet Ground States of the Hydrogen Molecule with Fixed Atoms and the Energy Difference Between the Two States as a Function of Atom Separation. The points on the two upper curves were obtained from the literature as follows:

- James, Coolidge, and Present, ref 45
- James and Coolidge, ref 44
- ▲ Slater, ref 46
- Herzberg, ref 48

The points on the difference curve were obtained from the difference between the singlet and triplet curves, while the dashed line is of the functional form shown.

Fig. 113. The Function $[1 - \exp(-\epsilon)]/[1 + 3 \exp(-\epsilon)]$ vs ϵ and the Approximation to It (Dashed Curve) Used.

finally to the following simple expression for the correction factor:

$$1 - I = \frac{(3.7kT/m^*A)^{N_d/B(m^*)^3}}{1 + N_d/B(m^*)^3}, \quad (15)$$

where $A = A_H/K^2$ ($= 0.068$ eV for silicon) and $B = B_H/K^3$ ($= 4.65 \times 10^{19}$ cm $^{-3}$ for silicon). These expressions give finally for the magnetic susceptibility per gram, $\chi = M/\rho H$,

$$\chi = C/T^{1 - N_d/B(m^*)^3}, \quad (16a)$$

where

$$C = \frac{N_d \beta^2}{\rho k} (3.7k/m^*A)^{N_d/B(m^*)^3} \times \left[1 + \frac{N_d}{B(m^*)^3} \right]^{-1}. \quad (16b)$$

Discussion and Comparison with Experiment

Silicon. — It is found experimentally⁵⁴ that the plot of χ vs $1/T$ is curved and has a smaller slope than $N_d \beta^2 / \rho k$. These two effects are both predicted by Eqs. (16). The power of the inverse T dependence is diminished by the term $N_d/B(m^*)^3$, and the constant C , which for no interactions is simply $N_d \beta^2 / \rho k$, is diminished by two factors, both increasing with N_d . Figures 114 and 115 show an attempt to fit the temperature dependence of the derived expression to the experimental data reported for silicon.⁵⁴ The data of Fig. 5, ref 54, have been replotted in log-log form, so that the slope of the resulting curve is $1 - N_d/B(m^*)^3$. The factor $N_d/B(m^*)^3$ thus obtained has then been compared with N_d reported from Hall measurements. It should be pointed out that there is a rather large uncertainty in the values of N_d obtained from Hall measurements, depending upon the assumptions which are made concerning the

⁵⁴E. Sonder and D. K. Stevens, *Phys. Rev.* 110, 1027 (1958).

Fig. 114. The Paramagnetic Susceptibility of Donors vs Reciprocal Temperature Plotted on Log-Log Paper. The data are obtained from ref 54.

- Specimen 743 (5×10^{18})
- Specimen 1407 ($12-20 \times 10^{17}$)
- ▲ Specimen 1262 ($6-10 \times 10^{17}$)
- Specimen 329 ($2-4 \times 10^{17}$)

mode of electron scattering and degree of degeneracy of the sample.⁵⁵ In Fig. 115 the values of N_d determined on the basis of assuming phonon scattering (circles) and impurity scattering (squares) have been plotted vs the factor $N_d/B(m^*)^3$ obtained from the slopes of the curves of Fig. 114. A straight line connecting the points should be proportional to $1/B(m^*)^3$. If the model is good, m^* should be the effective mass of an electron frozen on an arsenic donor in silicon.

⁵⁵ To obtain the donor density, N_d , from the Hall coefficient, R , the equation $N_d = (\mu_H/\mu)/Rec$ is used. (μ_H/μ) is the ratio of Hall to conductivity mobility, equal to $3\pi/8$ for spherical energy bands and phonon scattering. For the more complicated conduction band of silicon and for an admixture of thermal and impurity scattering, the ratio may vary between 0.8 and 1.9. See ref 54 and refs 28 and 29 therein for a fuller discussion.

Fig. 115. The Donor Density N_d Plotted vs $N_d/B(m^*)^3$. The points are from the experimental data shown in Fig. 114, while the straight lines are predicted by the theory for different values of the effective mass of electrons in donor states.

Lines for $m^* = 0.51, 0.53$, and 0.55 have been drawn on Fig. 115. The m^* calculated from the donor activation energy⁵⁶ and Eq. (1a) is 0.513. As can be seen, the agreement is fairly good for samples having less than 10^{18} donors/cm³. The deviation in a sample having 5×10^{18} donors/cm³ is quite large, but in this range the assumptions which entered this theory are not satisfied. (It might be pointed out that in the sample with 10^{18} donors/cm³ the maximum of the distribution of distances [Eq. (9)] occurs for such interatomic distances that the splitting energy is 0.0007 eV, which, together with the criterion $E = 2kT$, gives a temperature of about 4°K, below which this theory would tend to break down.)

Germanium. — In germanium the effective mass is much smaller than in silicon, and the donor levels are much closer to the conduction band. Moreover, the dielectric constant is greater; and so the donors interact at larger distances. In Table 19 is shown a comparison of the constants m^*A_H/K^2 and $(m^*)^3B_H/K^3$ for silicon and germanium. Since it is the ratio of N_d to the second

⁵⁶ F. J. Morin et al., *Phys. Rev.* 96, 833 (1954).

Table 19. Comparison of Constants Used in the Expression of the Magnetic Susceptibility

	H ₂	Si	Ge
$E = \text{ionization energy, ev}$	13.6	0.049	0.012
Dielectric constant	1	11.9	16
Effective mass (electron masses)	1	0.51	0.23
$m^* A_H / K^2, \text{ ev}$	9.66	0.0348	0.0087
$(m^*)^3 B_H / K^3, \text{ cm}^{-3}$	7.84×10^{22}	6.17×10^{18}	2.33×10^{17}

of these which determines the deviation from a linear dependence on $1/T$, it is evident that the situation in germanium corresponding to that which we have discussed in silicon arises in samples which are purer by a factor of 25. This means that the present discussion applies to germanium only when the concentration of impurities is less than about 5×10^{16} donors/cm³. It is in just such a specimen (5.5×10^{16} cm⁻³) that Bowers⁵⁷ has observed a slight paramagnetism at low temperature, with a slope less than one would expect for noninteracting donors. There actually seems to be a slight curvature in the data presented by Bowers,⁵⁷ which also is in qualitative agreement with the foregoing.

Conclusions

The magnetic susceptibility of donor centers distributed at random in a semiconductor has been calculated for the case in which interactions between pairs of donors is small but not negligible. A hydrogenic model was assumed for the donor center; the energy difference of singlet and triplet donor-molecule states was scaled from corresponding values for the hydrogen molecule. The difference, or splitting energy, was approximated by a mathematical expression which permitted the evaluation of certain integrals. Only the singlet and triplet ground states were retained in the partition sum, which included terms for a range of internuclear distances. Summing over the distance between donors and differentiation of the partition sum gave the final expression for the susceptibility.

Even though there are no adjustable parameters in the theory, agreement with experiment seems

fairly good in the case of silicon. The theory predicts an onset of pairing in germanium at a value which is also in qualitative agreement with experiment.

One of the results of this calculation is to raise some questions about the procedure of using the temperature-limiting slope of the Curie plot to obtain the donor density of the specimen. A sizable correction factor, of the order of 10 to 50%, seems to be required even when no large curvature is apparent in the data.

MAGNETIC SUSCEPTIBILITY OF ALUMINUM ANTIMONIDE

E. Sonder L. C. Templeton

Some preliminary results of measurements of the magnetic properties of AlSb are shown in Fig. 116. The data, unfortunately, are not as easy to account for in terms of electrons and holes freezing out on donor and acceptors, respectively, as were those for silicon.⁵⁸ If the susceptibility of the compensated sample is assumed to be predominantly the core diamagnetism of the pure compound, then it is impossible to explain the much smaller diamagnetism of the *p*-type sample. At best, only about 10% of the difference between the room-temperature values of χ for the two samples is due to the spin paramagnetism of the free holes. Moreover, if the difference were caused by a Curie-law paramagnetism, as would be expected for free holes with a very small freedom number, then the difference between the curves should become greater at somewhat lower temperatures. This is clearly not the case.

⁵⁷R. Bowers, *Phys. Rev.* 108, 683 (1957).

⁵⁸D. K. Stevens, W. J. Sturm, and J. H. Crawford, Jr., *Solid State Semiann. Prog. Rep.* Aug. 30, 1956, ORNL-2188, p 7.

A greater divergence, as the temperature drops below room temperature, would also be expected between the curves for the n -type sample and the compensated one if the difference were due to a diamagnetism of the form

$$\chi = \frac{n\beta^2}{3\rho kT} (3 - \langle f \rangle^2),$$

where the freedom number $\langle f \rangle$ is greater than $\sqrt{3}$. This also is not the case. It may be that a third contribution to the magnetic susceptibility, in addition to the free carrier and doping impurity contributions, is present and differs in different specimens. Whether this is due to contamination, surface-oxide film, or impurities that are electrically inactive is, of course, not known. It should also be pointed out here that the values for the donor and acceptor concentrations have not been measured by us but have been estimated from values given for the ingots from which the susceptibility samples were cut.

It is, of course, quite possible that the large amount of tellurium necessary to make AISb intrinsic or n -type causes formation of impurity bands which cause some of the unusual results. The possibility of banding is also suggested by

Fig. 116. Magnetic Susceptibility of Aluminum Antimonide as a Function of Temperature.

the fact that Curie plots of the low-temperature, paramagnetic tails of the curves for both the n - and p -type samples yield for the number of magnetic centers values that are a factor of 5 or more smaller than the values reported for the number of donors and acceptors, respectively.

INSULATING CRYSTALS

FAST-NEUTRON AND GAMMA COLORATION
IN KCl

C. M. Nelson

W. J. Pegram¹

In connection with radiation effects in solids, some studies have been made on fast-neutron-induced coloration in KCl. The growth rates of the *F* and *V* bands with Co^{60} and reactor irradiations have been compared in an effort to discover the added effect of fast neutrons. These irradiations were carried out near room temperature on KCl obtained from the Isomet Corporation. A few experiments have been made using KCl obtained from the Harshaw Chemical Company but will not be discussed here since there apparently was no large difference in behavior. The Isomet samples do not have any of the absorption band near 2130 Å usually encountered in unirradiated Harshaw material. Neutron bombardments were carried out in Hole 51 of the ORNL Graphite Reactor (8×10^{11} fast neutrons/sec), and the Co^{60} facility had a dose rate of 8×10^5 r/hr. The optical absorption

spectra were measured on the Cary model 14 spectrophotometer.

Both types of irradiation indicate that there may be three stages in the production of the *F* band and *V* bands. The initial rapid coloration (stage I) and the subsequent steady buildup (stage II) have been studied with x-ray and Co^{60} radiation facilities, particularly by Nowick² using NaCl. The present results using Co^{60} and fast neutrons indicate a later even slower buildup (stage III).

It was difficult to make an estimate of the ionization field in the reactor. For the purposes of this discussion, it was decided to adjust the exposure scale for the reactor irradiation (multiply exposure time by a factor of 5) thereby making the *F*- and *V*-band buildups in stage II approximately equal for the fast-neutron and Co^{60} irradiations. Using this assumption the growth of the *F* band is indicated in Fig. 117 and the *V* band in Fig. 118.

With the assumption made for the ionization field in the reactor, Fig. 117 indicates that the *F* band

¹Co-op employee.²A. S. Nowick, *Phys. Rev.* 111, 16 (1958).

Fig. 117. Growth of *F* Band with Co^{60} and Reactor Irradiation. Neutron bombardment time was multiplied by 5 for comparison with gamma irradiation.

risks more rapidly with fast-neutron bombardment than with purely ionizing radiation in stage I. Though the curves coincide during the first 5 min, a factor of 8 or 9 would be necessary to make the fast-neutron values correspond to the gamma-ray values near 60 min of equivalent gamma irradiation. The situation in the V-band region (Fig. 118) is quite different from the F-band growth. There is a band produced in this stage with a maximum at 2140 Å (5.80 eV) and a half width of 0.82 eV for both neutron- and gamma-irradiated

samples (Fig. 119). This band bleaches with continued irradiation as seen in Fig. 118, particularly with gamma irradiation. If a factor of 2 was used to multiply the fast-neutron time, the maximum of this band growth, that is, the point when it starts to bleach, is about the same for fast-neutron and gamma irradiations.

In stage II the F-band and V-band growth rates are about constant for both fast-neutron and gamma irradiations (Figs. 117 and 118). Using the factor of 5 for the fast-neutron bombardment time, the

Fig. 118. Growth of V Band with Co⁶⁰ and Reactor Irradiation. Neutron bombardment time was multiplied by 5 for comparison with gamma irradiation.

Fig. 119. Optical Absorption Spectrum of Irradiated KCl in Stage I.

F-band growth rate is slightly larger than the growth rate for gamma irradiation. However, the *V*-band growth rates are about the same. With the disappearance of the band at 2140 Å, there was a general rise in absorption from 1850 to 2400 Å (this is the reason why the *V*-band curve in stage I never went to zero).

The *F*-band growth rate is less in stage III than in stage II for both fast-neutron and gamma irradiations. It appears that the change from stage II to stage III occurs later for the fast-neutron irradiation using the time factor of 5. If a value less than 5 had been chosen for this factor in order for the transition between the stages to coincide, the growth rate for fast-neutron irradiation would be larger than for gamma irradiation. Notice in Fig. 117 that the growth rate for fast-neutron irradiation is less than for gamma irradiation in stage III. However, Fig. 118 shows that the *V*-band growth is quite different from the *F*-band growth in stage III. The transition from stage II to stage III appears to be earlier for fast-neutron bombardment than for gamma irradiation. Also the *V*-band growth rate for fast-neutron bombardment is larger than for gamma irradiation.

Evidently, reactor bombardment is causing some difference in the coloration of KCl. The absorption spectra in the *V*-band region show the effect of the fast neutrons. An apparent maximum occurs at 2140 Å after 47 hr in the reactor, whereas the

maximum occurs at 2080 Å after 628 hr in the Co^{60} source (Fig. 120). The *F* band for these samples was too intense to be measured. However, subtracting the gamma-colored spectrum from the neutron-colored spectrum indicates that there is an absorption maximum at 5.4 eV (2300 Å) which is more abundant after fast-neutron bombardment compared to gamma irradiation. Also there is the indication of a maximum at 6.5 eV. This excess neutron coloration was estimated in the three stages by irradiating samples for "equivalent" doses, adjusting the *F*-band maxima to be equal, and then subtracting the gamma-colored spectrum from the neutron-colored spectrum. The results for the three stages are given in Fig. 121. There is apparently no difference in stage I. However, in stage II the difference curves show maxima at 5.4 eV and possibly 6.5 eV. Stage III shows the growth of the 5.4-eV maximum over stage II. The situation near 6.5 eV is not clear in stage III. It may be that there is other absorption developed below 1900 Å.

Indications of a fast-neutron effect in the *F*-band region can be noted in Fig. 121. There is an increase of optical absorption near 2.5 eV (5000 Å) in comparing stage III with stage II. This is also apparent near 1.7 eV (7300 Å). However, a negative absorption (i.e., depressed in fast-neutron bombardments) may also be present since there is an increase in this negative absorption near 2 eV

Fig. 120. Optical Absorption Spectrum of Irradiated KCl in Stage III, Showing the Fast-Neutron Effect.

(6000 Å) in comparing stage III with stage II. These results in the *F*-band region are not too conclusive. However, there is probably some fast-neutron effect, since the *F*-band maximum did not shift in value compared to gamma irradiation.

Perhaps the best illustration of the difference in fast-neutron bombardment is given in Fig. 122, where the ratio F/V is plotted for the various stages. Again the time factor of 5 was used for neutron bombardment. After the initial part in stage I, the ratio after fast-neutron bombardment is quite divergent from the gamma-ray behavior. Another observation which can be made from Fig. 122 is that the *F* and *V* bands grow somewhat independently of each other in all stages. Though the ratio for fast-neutron bombardment in stage I is apparently constant, it is known, as mentioned above, that the unidentified band at 2140 Å grows and bleaches in this stage, whereas the *F* band always increases (Fig. 117).

VACUUM ULTRAVIOLET ABSORPTION STUDIES OF IRRADIATED SILICA AND QUARTZ

C. M. Nelson W. J. Pegram¹

In addition to the optical absorption bands discussed previously, there are bands developed in fused silica and crystalline quartz in the vacuum ultraviolet region. Mitchell and Paige³ discovered a band developed with reactor bombardment at 7.6 eV or 1630 Å in both fused silica and crystalline quartz. A band at 7.15 eV or 1730 Å was observed with x-ray irradiation but not with reactor bombardment. Since this band has a maximum extinction coefficient of 0.3 mm^{-1} for the x-ray dose and did not develop with neutron bombardment, this band at 7.15 eV may be associated with an impurity atom and not with a lattice

³E. W. J. Mitchell and E. G. S. Paige, *Phil. Mag.* 1, 1085 (1956).

Fig. 121. Excess Neutron Coloration Obtained by Subtracting Gamma-Colored Spectrum from Neutron-Colored Spectrum.

Fig. 122. Variation of F/V Band Ratio with Co^{60} and Reactor Irradiation. Neutron bombardment time was multiplied by 5 for comparison with gamma irradiation.

defect color center. These optical absorption measurements were made with a spectrograph using the variation in film darkening as an indication of the absorption in the sample.

A vacuum ultraviolet spectrophotometer⁴ has been constructed at ORNL in order to investigate the color centers developed in this spectral region by irradiation. This instrument uses a 1P28 photomultiplier tube coated with sodium salicylate as a detector and covers the spectral region of 1000 to 2400 Å. Consequently the data obtained from this instrument overlap the data obtained from the Cary model 14 (1850 to 26,000 Å) used for previous optical absorption studies.

The materials used in this study were fused quartz,⁵ high-purity synthetic fused silica,⁶ natural crystalline quartz,⁷ and synthetic crystalline quartz.⁸ Samples were irradiated in a Co^{60} source having a flux of 8×10^5 r/hr. In all curves of extinction coefficient vs wavelength

presented here, the absorption of the unirradiated material has been subtracted. Low-temperature optical bleaching experiments were conducted with the sample immersed in liquid nitrogen. Two mercury lamps having a different spectral distribution were used. The chief difference between these lamps is that the 4-w germicidal lamp had an ordinary glass envelope with a short-wavelength cutoff near 3000 Å, whereas the 250-w Uviarc lamp had a fused-silica container which transmits light of wavelength below 2000 Å. Thermal bleaching experiments were carried out in air using a Leeds and Northrup DAT program controller at temperatures up to 1000°C.

Preliminary work with fast-neutron bombardment confirmed the observations of Mitchell and Paige³ concerning the appearance of the 7.6-eV band in both fused silica and crystalline quartz. However, due to the very high extinction coefficient (about 20 mm^{-1}) even for 10^{17} nvt fast, no further experiments were made in our studies. Previous research⁹ had indicated the similarity in the spectra observed after neutron bombardment and Co^{60} gamma irradiation except for the much less total absorption for gamma-irradiated specimens. On this basis it was felt that studies should be concentrated on gamma-irradiated samples for ease in handling (thicker samples could be used), better

⁴C. M. Nelson et al., *Solid State Ann. Prog. Rep.* Aug. 31, 1958, ORNL-2614, p. 25.

⁵Obtained from Amersil Company, Inc. (optical grade 1).

⁶Obtained from Corning Glass Works (7940) and Thermal American Fused Quartz Company (Vitreosil O.S.).

⁷Obtained from Cambridge Thermionic Corporation.

⁸Secured through the courtesy of C. S. Brown, G.E. Co., Ltd., England, and J. M. Stanely, U.S. Army Signal Research and Development Lab. (originally grown by the Clevite Research Center).

⁹C. M. Nelson and J. H. Crawford, Jr., *Phys. and Chem. Solids* (to be published).

controls over experimental conditions, and absence of induced radioactivities.

It soon became evident, after these studies were initiated, that there were a number of absorption bands in the region 6 to 9 ev. In an effort to analyze and identify these bands, a Lorentzian absorption curve was assumed for each band and a method of curve fitting to give the observed data was used. Fortunately, annealing and bleaching experiments changed the shape of the total curve so that certain bands became prominent. With these assumptions, some generalized statements can be made as to the properties of these bands. It appears that the major absorption bands have maxima at 7.65, 8.05, and 8.20 ev, and there are indications of minor absorption bands at 7.25, 7.40, 7.85, and 7.95 ev. These minor bands were difficult to establish because of their relatively low intensity and proximity to the major bands. An example of a total analysis is given in Fig. 123 for irradiated synthetic crystalline quartz from Clevite.

The 7.65-ev band (the *E* band of Mitchell and Paige³) is found in all samples of irradiated quartz and silicas. Though it is not the most intense band initially, continued irradiation above 10^9 r apparently produces this band in higher yield than the others. Neutron-bombarded samples also indicated that this band was the most prominent. Since the intensity of this band is not the same

Fig. 123. Absorption Spectrum of Gamma-Irradiated Clevite Quartz, Showing the Result of Fitting Lorentzian Absorption Curves for Individual Absorption Bands to Make Up the Composite Curve.

for different samples after an equivalent irradiation, it is apparently structure sensitive. The growth of this band with gamma irradiation of quartz and silica is shown in Fig. 124. The optical and thermal bleaching behavior of crystalline quartz and fused silica is given in Figs. 125 and 126, respectively. In crystalline quartz

Fig. 124. Growth of *E* Band with Gamma Irradiation of Fused Silica and Crystalline Quartz.

the 5.4- and 5.9-ev bands do not develop with gamma irradiation as they do in fused silica as discussed above.¹⁰ Even though these bands are absent, bleaching at 78°K with the mercury lamps does influence the vacuum ultraviolet bands (Fig. 125). The germicidal lamp (glass envelope) tended to enhance the 7.65-ev band, whereas the Uviarc lamp (fused-silica envelope) tended to decrease the 7.65-ev band. Heating the sample at 250 and 300°C for 30 min caused an increase of the 7.65-ev band, while higher temperature treatments decreased this band.

The vacuum ultraviolet spectra of gamma-irradiated Corning fused silica are shown in Fig. 126. Though the unirradiated spectrum of this sample was unknown, it was assumed that all the induced absorption was gone after heating at 700°C for 30 min, and this spectrum was subtracted from the other observed spectra to obtain the curves of

¹⁰ C. M. Nelson and R. A. Weeks, "Trapped Electrons in Irradiated Silica and Quartz." See abstract, this report.

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Fig. 125. Optical and Thermal Treatments of Irradiated Clevite Quartz.

Fig. 126. Bleaching with the mercury lamps at 78°K apparently causes a change in the intensity of the 7.65-ev band that is similar to but much less than that observed in crystalline quartz (Fig. 125). As discussed above,¹⁰ the 5.4- and 5.9-ev bands are influenced much more strongly by these treatments. In contrast to the behavior of the 7.65-ev band in quartz (Fig. 125), heating the fused-silica sample at 250°C for 30 min caused a decrease in the 7.65-ev band. Higher temperature treatments continued to reduce this band.

As can be seen from Figs. 125 and 126, other absorption bands are developed in fused silica and quartz after gamma irradiation. The most prominent is the 8.20-ev band, with the 8.05-ev band indicated by subtracting the observed spectra

after different treatments (e.g., in Fig. 126 subtract the spectrum after heating at 450°C from the spectrum after heating at 250°C). Apparently the 8.20-ev band is thermally more stable than the 8.05-ev band in this sample.

Evidence for an absorption band at 7.40 ev is gained from curve fitting (Fig. 123) and apparent growth by heating between 600 and 700°C (Fig. 125) in some samples. Another band, noted at 7.85 ev in Fig. 123, became prominent in samples of irradiated Vitreosil O.S. fused silica and natural quartz. Other bands at 7.25 and 7.95 ev (Fig. 123) are suggested to explain various optical and thermal bleaching behavior.

On the basis of some indirect evidence, Mitchell and Paige³ have suggested that the 7.65-ev band

Fig. 126. Optical and Thermal Treatments of Irradiated Corning 7940 Fused Silica. The plotted points were obtained by subtracting the spectrum after 30 min at 700°C from the other spectra.

was the result of a trapped hole on an interstitial oxygen. As a result of numerous complementary experiments, it has been concluded¹¹ that this band is associated with a broad electron spin resonance system with a g value characteristic of a trapped hole. Since this becomes the most prominent band after long gamma irradiation or fast-neutron bombardment, it is suggested that the color center responsible is an interstitial oxygen ion (O^-). Also, this band is the most stable upon

¹¹C. M. Nelson and R. A. Weeks, *Bull. Am. Phys. Soc.* [2]4, 158 (1959).

thermal annealing (except for the 7.40-ev band increasing in some cases). The results presented here indicate that there are other absorption centers present, but there is no indication as to what defects may be associated with them.

It should be pointed out that the 5.9- and 7.65-ev bands do not develop together (witness the great difference between fused silica and crystalline quartz), nor do they bleach and anneal together (notice particularly that only the 7.65-ev band is left after a 500 to 550°C anneal, Fig. 126). Thus, though the 5.9-ev band has been associated with

a trapped electron and the 7.65-ev band with a trapped hole, the two defect centers do not appear to be necessarily complementary to each other. Therefore, other defects are apparently necessary in a complete model.

The following is an abstract of a paper submitted for publication.

Trapped Electrons in Irradiated Silica and Quartz.

I. Optical Absorption.¹² C. M. Nelson and R. A. Weeks. — Previous studies¹³ have associated the 2100-Å absorption band with an electron spin resonance system developed in silica and quartz after irradiation. Evidence derived from bleaching studies at 78°K after gamma irradiation is associated with another ESR system (described in "Trapped Electrons in Silica and Quartz. II. Electron Spin Resonance"). After 10⁹ r, G.E., Ltd., synthetic quartz slowly develops this band rather than the 2100-Å band. The 2300-Å band is also produced in high-purity fused silica as shown by bleaching at 78°K with a 4-w germicidal mercury lamp (glass envelope); and as the 2300-Å band decreases, there is a corresponding increase in the 2100-Å band. Although the 2100-Å band is dominant in silica after irradiation, bleaching experiments indicate the 2300-Å band is at least three times the amplitude found in synthetic quartz for an equivalent dose. Bleaching with a Uviarc mercury lamp (silica envelope) reverses the process (the 2100-Å band decreases and the 2300-Å band increases) at 78°K in silica. With G.E., Ltd., quartz, bleaching with the germicidal lamp at 78°K decreases the 2300-Å band, but with no apparent increase in the 2100-Å band. The conversion of the 2300-Å to the 2100-Å band which occurs in silica at 78°K apparently will occur near 50°C with the germicidal lamp for the G.E. synthetic quartz. However, this conversion does seem to take place in irradiated natural quartz at 78°K where there is already some 2100-Å band present. Annealing quartz between 250 and 300°C causes an increase in the 2100-Å band, but it completely disappears by 450°C. Synthetic silica always shows a decrease in the 2100-Å band upon annealing.

IRRADIATION EFFECTS AND SHORT-RANGE ORDER IN SILICA AND QUARTZ

R. A. Weeks C. M. Nelson

Electron spin resonance (ESR) measurements¹⁴ have shown that for neutron doses greater than 10¹⁹ fast neutrons/cm² the ESR spectra observed at room temperature are the same in all the various fused silicas and single crystals on which

observations have been made. It was also shown that the three ESR lines observed in silicas were the same as the ESR lines observed in the single crystals and that these paramagnetic centers were due to irradiation-produced ionization states of the quartz structure and not to impurity atoms.

In a free paramagnetic ion the transition energy of the Zeeman levels is determined by the spectroscopic splitting factor given by the Lande formula.¹⁵ If the paramagnetic ion is introduced into a solid, the internal interactions perturb the Zeeman levels and the Lande formula is no longer applicable. For the spin states only, the energy relation is still of the form $h\nu = g\beta H$, where h is Planck's constant, ν is the frequency of the oscillating magnetic field perpendicular to the spin-orienting field H , β is the Bohr magneton, and g is the spectroscopic splitting factor. The introduction of paramagnetic centers into a normally diamagnetic crystal and the ESR spectra which result may give, through a knowledge of g , a microscopic model of the crystalline field surrounding the center.¹⁶

In a polycrystalline or an amorphous glasslike material, the observed line is the envelope of the line in the single crystal when averaged over random orientation of the single crystal. Information obtained from such an envelope is of little use in constructing a model of the paramagnetic center, but when identifying a line observed in a single crystal with one observed in a polycrystal it is necessary. Such a comparison can be made experimentally by crushing a single crystal. This procedure was used in identifying a group of ESR lines, produced by neutron irradiation, in a single crystal of quartz with a line observed in silica produced by the same irradiation.¹⁴ Knowing the values of the spectroscopic splitting factor it is possible to calculate the line expected for a polycrystalline or fused material. A calculation

¹²Submitted for publication in the *Journal of the American Ceramic Society*.

¹³C. M. Nelson and J. H. Crawford, Jr., *Bull. Am. Phys. Soc.* [2]3, 136 (1958).

¹⁴R. A. Weeks, *J. Appl. Phys.* 27, 1376 (1956).

¹⁵W. Gordy, W. V. Smith, and R. F. Trambarulo, *Microwave Spectroscopy*, John Wiley and Sons, New York, 1953.

¹⁶D. J. Ingram, *Spectroscopy at Radio and Microwave Frequencies*, Butterworth Publications, Ltd., London, 1955.

of this type has been performed for a cupric ion in silica, assuming axial symmetry.¹⁷

A similar calculation for one of the paramagnetic defects of the quartz system has been made. The calculated line shape is compared with the line shape observed in various silicas which have been given a variety of irradiation treatments. A similarity in the short-range order of some of the silicas and the order in a single crystal is suggested; likewise, a similarity in the crystalline field interacting with the paramagnetic defects in one of the silicas is found to be similar to the field in a heavily irradiated silica or single crystal. The experimental results indicate that the short-range order in the heavily irradiated specimens of fused silica and single crystals of quartz is identical and that it is different from that initially present in most silicas.

In the single crystal the defect corresponding to the one observed in the silicas was found to have the following eigenvalues for the spectroscopic splitting factor:

$$g_1 = 2.0018, \quad g_2 = 2.0006, \quad g_3 = 2.0003,$$

where subscripts refer to the coordinate system of the g tensor. The relative accuracy of these values was ± 0.0001 , the absolute accuracy ± 0.0005 . There are six possible orientations of the g tensor in the unit cell. These orientations with respect to the crystalline axis were also determined for this g tensor.¹⁸

In calculating the envelope shape expected for the silica state it has been assumed that the line shape is of the Lorentzian form. The contribution of each fraction of centers, $-dN/dH$ from

$$\frac{h\nu}{g_1\beta} \leq H_0 \leq \frac{h\nu}{g_3\beta},$$

at some field H , can be found by integrating from

$$H_1 = \frac{h\nu}{g_1\beta} \text{ to } H_3 = \frac{h\nu}{g_3\beta};$$

thus

$$A(H) = \int_{H_1}^{H_3} \frac{T_2/\pi}{1 + 4\pi C^2 T_2^2 (H_0 - H)^2} \times \frac{dN}{dH_0} dH_0. \quad (1)$$

The ratio dN/dH_0 is evaluated from

$$\frac{h\nu}{g_1\beta} \leq H_0 < \frac{h\nu}{g_2\beta}$$

and

$$\frac{h\nu}{g_2\beta} < H_0 \leq \frac{h\nu}{g_3\beta},$$

and in the region of $H_0 = h\nu/g_2\beta$ the finite line amplitude eliminates the singularity. Because of the difficulty of obtaining an analytic solution of Eq. (1), a numerical integration was performed by using nine values of H_0 and 12 values of H .

In Fig. 127 a comparison is made between the envelope shapes observed in silica for various irradiations and the shape calculated from the single-crystal parameter for the same center.

Fig. 127. The Shape of the Envelope Calculated for $w = 0.2$ oersted Is Compared with the Envelope Shape Observed in Various Silicas Given Different Irradiation Treatments.

The gamma-ray-irradiated silica exhibits the best agreement with the calculated envelope shape. Consideration was given to the effects of center concentration, type of irradiation, temperature of irradiation, and magnetic interactions with other paramagnetic centers. The effects of these parameters on the envelope were found to be less than that of the crystalline field.

¹⁷R. H. Sands, *Phys. Rev.* **99**, 1222 (1955).

¹⁸R. H. Silsbee and R. A. Weeks, *Solid State Semiann. Prog. Rep.* **30**, 1956, ORNL-2188, p 105.

Figure 128 shows the effect of heat treatment on a heavily irradiated single crystal. Curve I of Fig. 128 is characteristic of silica or crystals after a neutron dose $\geq 5 \times 10^{19}$ nvt. Curve II of Fig. 128 results after the indicated heat treatment. There is only a small decrease in the intensity of the line after the treatment. The change in concentration of other paramagnetic centers is also small. The change in the envelope shape is therefore not due to a change in the magnetic interactions of this center with similar or dissimilar paramagnetic centers.

Fig. 128. The Shape of the Envelope in a Heavily Irradiated Single Crystal as a Function of Annealing. The change begins during the 450°C anneal. The amplifier gain for III is $\times 10$.

The remaining interaction which can determine the line shape in the silicas is that of the crystalline field interacting with the paramagnetic center. If this is the case, then the alteration of line shape with increasing neutron dose in the normal silicas (Corning 7940, Amersil O. G. 1) and in the single crystal is due to a change in the crystalline field. This change is apparently correlated with the change in density.¹⁹ For a

neutron dose $> 5 \times 10^{19}$ fast neutrons/cm², the line shape does not alter nor does the density. Annealing at 450°C for 30 min initiates a change in the envelope line shape (Fig. 128) which is then indicative of a reordering of the neighboring atoms which gave rise to the crystalline field interactions. Further annealing at successively higher temperatures continues the reordering process, and after 30 min at 550°C the process is complete (Fig. 128, curve III). The line shape after this anneal is the same as that observed in gamma-ray-irradiated normal silica and is in agreement with the line shape calculated from the single-crystal parameters.

Although the orientation with respect to the crystalline axis and the eigenvalues of the g tensor are known from measurements on a single crystal, this information has not been adequate to define the nature of this center. The g tensor is orthorhombic, with six possible sites in the unit cell. It has been established that this center is a defect state of the basic Si-O tetrahedra.¹⁴ It has been suggested that this defect is an electron trapped at an oxygen-ion vacancy. Assuming that this is the case, the interaction of the electron with the nearest neighbor atoms is the dominant effect in determining the envelope shape in the silicas. The comparison of the envelope shape in gamma-ray-irradiated silica, in which the defects are assumed to have a random distribution, with the shape calculated from single-crystal parameters shows that they are in good agreement. This agreement of observed and calculated envelope shape means that in these silicas the interaction of the surrounding atoms with the defect is the same as in the single crystal. Another way of stating this result is to say that the variation of the orientation of the Si-O tetrahedra with respect to adjacent tetrahedra in the silica is small compared with the extent of the interaction of the defect with the surrounding atoms. The trapped electron could be considered as occupying a molecular orbital connecting the two adjacent silicon atoms. The g tensor would then be determined primarily by the way in which these Si atoms were affected by the vacancy and the three remaining O atoms on each silicon. The approximate distance from the vacancy to the nearest O atoms is ~ 2.6 Å and to the next nearest shell of oxygen atoms is ~ 3.2 Å (ref 20). From

¹⁹M. C. Wittels, *Phys. Rev.* 93, 1117 (1954).

²⁰R. W. G. Wyckoff, *The Structure of Crystals*, The Chemical Catalog Company, Inc., New York, 1931.

these atom spacings it seems reasonable to conclude that in the silicas the orientation of the Si-O tetrahedra with respect to each other varies slowly with respect to a distance between 5 and 10 Å. Thus, around any point in the silica the structure of the atoms is similar to that in a crystal within a sphere of diameter ≤ 10 Å.

The implication of the envelope shape data is that short-range order exists in certain silicas, for example, Corning 7940 and Amersil. This order probably extends over the Si-O tetrahedra surrounding any point in the material and may be characterized as an alpha phase.

Heavy neutron irradiation destroys this order in these silicas as it does in a single crystal. If there is an ordering process induced by the irradiation, it does not produce the same order that existed in the unirradiated silica or quartz. This short-range order may be similar to the tridymite phase. A short anneal at 550°C can re-establish the short-range order existing in most silicas prior to irradiation.

The following are abstracts of papers submitted for publication.

Defects of the Quartz System Produced by Neutron Irradiation.²¹ R. A. Weeks. — A comparative study of the electron spin resonance (ESR) spectra of neutron-irradiated high-purity silica and quartz single crystals confirms the presence of three or probably four defects of the quartz system which are paramagnetic. In quartz, gamma-ray irradiation not only ionizes defects of the lattice already present, but also impurities. The saturation concentration of the lattice defects is of the same order as the impurities. Prolonged neutron irradiation ($> 5 \times 10^{18}$ fast neutrons/cm²) increases the concentration of the lattice defects by at least an order of magnitude over the impurity concentration, thereby separating the two kinds of defects. Annealing of the paramagnetic lattice defects indicates the probable existence of at least two other defects of the lattice.

The defect models suggested by the ESR spectra are as follows: The single line²² $g = 2.0006$ is due to

an electron trapped at an oxygen-ion vacancy, in agreement with the $\Delta g < 0$. The large increase observed for this line upon annealing (300°C, 30 min) a specimen irradiated at low temperatures suggests that two electrons may be trapped at such a vacancy and that this center is then stable at room temperature (although annealing has been observed in a specimen held at room temperature for several months). The anisotropy of a double line centered on the $g = 2.0006$ line, separation ~ 0.4 oersted, suggests an Si with three O and a trapped electron. The line $g = 2.0065$ also increases with this anneal. Although confirmatory evidence from the anisotropy of the line is lacking, the only available hole traps ($\Delta g > 0$) excluding impurities are interstitial oxygen ions. A defect model for the neutron-specific line $g = 2.0020$ has not been devised. The anisotropy of this line indicates that it is a hole ($\Delta g > 0$).

The Electron Spin Resonance of the 2300-Å Absorption Band in Irradiated Quartz.²³ R. A. Weeks and C. M. Nelson. — Several systems of ESR (electron spin resonance) lines have been observed in gamma-ray-irradiated natural and synthetic crystals. The correlation of one system of lines with an optical absorption band at 2300 Å, also observed in the crystals, has been established. The correlation was made by observations on irradiated crystals of differing origin and by bleaching experiments carried out at 78°K. The system of ESR lines is composed of two lines when the c axis [00.1] is parallel to H , and for the [10.0] orientation six lines can be distinguished. Due to the complexity of the spectrum and the small anisotropy, accurate measurements of the g tensor orientation and eigenvalues have not been made; estimates of the eigenvalues are $g_1 \approx 2.004$, $g_2 \approx ?$, $g_3 \approx 2.0020$, and for the [00.1] orientation g is 2.0007 and 2.0009. This ESR system and the 2300-Å band have also been observed in neutron-irradiated crystals and grow with increasing irradiation. The presence of the optical band in irradiated high-purity silica and its growth with continuing neutron irradiation apparently eliminate impurity ionization states as a source of the defect. A comparison of the anisotropy and Δg (ref 24) of this center with similar quantities for the ESR system tentatively associated with an electron trapped at an O vacancy^{14,25} suggests that this

²¹ Paper presented at 13th Annual Frequency Control Symposium, Asbury Park, N.J., May 12-14, 1959.

²² These terms are only applicable for an orientation of crystal in which the c axis is parallel to the magnetic field H .

²³ Submitted for publication in the *Journal of The American Ceramic Society*.

²⁴ $\Delta g = g_{\text{center}} - g_{\text{free electron}}$

²⁵ F. J. Adrian, *Phys. Rev.* 107, 488 (1957).

defect has a similar environment. The separation of the two lines for the $[00.1]$ orientation, $H \approx 0.4$ oersted, is in agreement with the difference in angle that two of the Si-O bond directions make with the $[00.1]$ direction. It is suggested that this defect may be due to an electron localized in an unsaturated silicon bond.

IRRADIATION EFFECTS IN NONMETALLIC CRYSTALS

M. C. Wittels

F. A. Sherrill

Introduction

Nonmetallic crystals, as a group, are exceedingly difficult to classify due to the wide diversity of crystal structures and complexity of chemical compositions. For these same reasons it is clear to see why a systematic understanding of the effects of irradiation on this group of crystals is not easily attainable. This report consists of a brief review only of the results for a small diverse group of crystals irradiated in core positions (C-38 and C-28) of the Low-Intensity Test Reactor.

The materials under consideration are oxides, mixed oxides, and silicates in which the cation components, for the most part, have low thermal-neutron absorption cross sections. This nuclear characteristic, together with the refractory nature of the crystals, gives the materials a potential reactor utility.

Experimental Method

Conventional x-ray techniques, including the use of Weissenberg, Buerger-precession, and Laue methods on small single crystals, were employed. The induced radioactivity was kept at a minimum level so that the standard film methods could be employed without the extraneous shielding that is often needed to reduce or eliminate background fogging. Similarly, Debye-Scherrer patterns were taken when single crystals were not available. In addition to these normal film methods a special diffractometer apparatus²⁶ was employed in studying larger single crystals.

The greater part of these studies was related to the damage produced by fast neutrons, but a few isolated examples of fission-fragment and heavy-charged-particle irradiations were examined as

well. All of these irradiations were performed at approximately 85°C in a water-cooled facility.

Effects in Crystals Containing Beryllium

The remarkable irradiation stability of the moderating material BeO has been extensively reported elsewhere²⁷ and will be only briefly mentioned here. Powder samples bombarded with fast fluxes up to 1.8×10^{20} neutrons/cm² showed no x-ray line broadening, although there is a very small lattice expansion (0.2%) of the c_0 axis, and the a_0 parameter remains unchanged. The mixed oxide BeAl₂O₄ (chrysoberyl) is also very stable under fast-neutron bombardment with integrated fluxes up to 8.1×10^{20} neutrons/cm². Single-crystal diffraction patterns remain sharp throughout this range of irradiations. An interesting structural feature of this material is the complete dominance of oxygen ions in the lattice, which are arrayed in a nearly perfect hexagonal close packed system. This close packing would be expected to result in measurable lattice parameter shifts if atomic displacements were trapped in interstitial positions, and this effect would be enhanced if the large oxygen ion comprised the trapped nuclei. The expansions of the three orthorhombic axes after irradiation with 3.6×10^{20} neutrons/cm² are 0.43% in a_0 , 0.55% in b_0 , and 1.05% in c_0 , respectively. Laue transmission photographs of BeAl₂O₄ after three dosages of irradiation are shown in Fig. 129. Note the development of a diffuse scattering pattern at small and moderate angles that is superimposed on the normal Laue pattern. This type of scattering is not of thermal origin and is commonly observed in crystals containing irradiation-induced defects. Although the scattering lies outside the zones of selective reflection, its high degree of symmetry related to the parent matrix is suggestive of scattering due to inhomogeneous strains developed through the trapping of interstitial atoms at statistical positions of the crystal lattice. Phenacite, Be₂SiO₄, is stable after irradiation dosages up to 8.1×10^{20} neutrons/cm² and also exhibits diffuse scattering patterns in transmission photographs (Fig. 130) of heavily irradiated specimens. Unlike

²⁶F. A. Sherrill, M. C. Wittels, and T. H. Blewitt, *J. Appl. Phys.* 28, 526 (1957).

²⁷J. R. Gilbreath and O. C. Simpson, *Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, paper 621 (1958).

Fig. 129. BeAl_2O_4 (Chrysoberyl). Laue transmission photographs, x-ray beam parallel to a axis; (a) after irradiation with 2.8×10^{20} neutrons/cm², (b) after irradiation with 3.6×10^{20} neutrons/cm², and (c) after irradiation with 8.1×10^{20} neutrons/cm².

Fig. 130. Be_2SiO_4 (Phenacite). Laue transmission photographs, x-ray beam parallel to c axis; (a) after irradiation with 4.53×10^{20} neutrons/cm², (b) after irradiation with 6.3×10^{20} neutrons/cm².

BeAl_2O_4 , however, this crystal has an unusually open structure, with open channels roughly parallel to c_0 , much like alpha-quartz.²⁸ And similar to the anisotropic behavior of quartz²⁸ under neutron bombardment, Be_2SiO_4 exhibits an anisotropic expansion in the same direction. After irradiation with 4.5×10^{20} neutrons/cm² the a_0 expansion

is 1.12%, while no change is measurable in c_0 . This extreme anisotropic behavior is most likely related to the open channels of the structure as well as to the directional binding forces within the lattice, which are more amenable to expansion in the a_0 direction.

As a result of neutron bombardment, the least stable crystal structure in this group under discussion is $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (beryl), which is

²⁸M. C. Wittels, *Phil. Mag.* 2, 1445 (1957).

very similar to quartz and phenacite in having open channels parallel to the c axis. This crystal becomes amorphous following bombardments in excess of 6×10^{20} neutrons/cm² when all single-crystal reflections disappear and all that remains in the diffraction pattern is a broad diffuse ring, characteristic of amorphous matter. Prior to the complete destruction of long-range order, at lower dosages of irradiation, beryl expands anisotropically nearly to the same extent as quartz.²⁸ After irradiation with 2.8×10^{20} neutrons/cm², the expansion of a_0 is 2.70%, while the distention of c_0 is 0.70%: about a factor of 4 lower. It is believed that the open c -axis channels in this crystal, as in those previously discussed, furnish ideal sites for trapping displacements that result in an anisotropic expansion. This extreme distention results in a highly strained and distorted lattice, giving smeared-out x-ray reflections (Fig. 131) with successive dosages of irradiation and a gradual reduction of long-range order.

Irradiation-Induced Amorphism in Silicates

The $[\text{SiO}_4]$ tetrahedral unit is the basic building block in silicate crystal structures. Since silicates are also common glassy bodies, it is

apparent that the rupture of silicon-oxygen bonds and the subsequent distortion of the arrangement of the $[\text{SiO}_4]$ tetrahedra resulting from fast-neutron bombardment might tend to produce amorphous silicates. If the process is a progressive one that develops with increasing irradiation dosages, one observes the gradual reduction of long-range order, a depression in x-ray peak intensities, and eventually the appearance of the diffuse halo that accompanies the growth of the amorphous material within the skeletal crystal matrix. In the early stages of the process the nonrandom, symmetrical, diffuse scattering that was described in the previous section as arising from inhomogeneous lattice strains and statistically trapped displacements is observed. An example of this effect is shown in Fig. 132 of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (garnet). Bombardment with 6×10^{20} neutrons/cm² produces amorphism in this crystal. The smearing of x-ray line profiles is exhibited in Fig. 133 for $\text{Al}_2(\text{OH})_2\text{SiO}_4$ (topaz), through a sequence of Weissenberg patterns. Diffractometer measurements on single crystals irradiated with 4.5×10^{20} neutrons/cm² showed axial expansions for a_0 , 2.87%; b_0 , 0.53%; and c_0 , 2.05%. With these large lattice parameter shifts it is not surprising that x-ray reflections

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Fig. 131. $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (Beryl). Laue transmission photographs, x-ray beam parallel to c axis; (a) unirradiated, (b) after irradiation with 2.8×10^{20} neutrons/cm².

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Fig. 132. $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Garnet). Laue transmission photographs, x-ray beam parallel to a axis; (a) un-irradiated, (b) after irradiation with 2.53×10^{20} neutrons/cm².

Fig. 133. $\text{Al}_2(\text{OH})_2\text{SiO}_4$ (Topaz). Weissenberg photographs, zero level (0 k l) projection; (a) unirradiated, (b) after irradiation with 3.6×10^{20} neutrons/cm², (c) after irradiation with 4.5×10^{20} neutrons/cm².

are heavily broadened. After irradiation with 6×10^{20} neutrons/cm² this crystal also becomes completely amorphous.

A third example of radiation-induced amorphism in silicates is ZrSiO_4 (zircon), which is completely disordered after irradiation with 6×10^{20}

neutrons/cm². Here also the progressive growth of amorphous regions within a distended crystal matrix is seen after successive lower dosages of irradiation. Annealing a crystal at 1600°C which is only partially amorphous after irradiation with 3.6×10^{20} neutrons/cm² produces recrystallization

on the skeletal single-crystal matrix to a more perfect structure. This is exhibited in the precession photographs shown in Fig. 134.

Oxides with a Higher Degree of Radiation Stability

Single crystals of MgO , Al_2O_3 (sapphire), and TiO_2 (rutile) have been subjected to integrated fast-neutron fluxes in excess of 10^{20} neutrons/cm². Preliminary studies indicate that TiO_2 is the most stable material of the three, because single-crystal diffraction patterns taken after irradiation with 1.1×10^{20} neutrons/cm² show no lattice distortions or imperfections and no lattice parameter shifts, within the limits of measurement. Exposure of MgO to 1.8×10^{20} neutrons/cm² produces a small lattice expansion (0.17%), but the over-all lattice perfection is little altered. Sapphire (Al_2O_3) was irradiated to a higher dosage, 6×10^{20} neutrons/cm², and showed significant lattice parameter shifts, but, again, single-crystal diffraction patterns show that a high degree of perfection is retained. After this dosage, a_0 expands 0.3% and c_0 lengthens 0.45%.

Effects in Crystals Due to Thermal-Neutron Reactions

Crystals which contain fissionable nuclei as constituents of their lattices are interesting materials from a radiation damage viewpoint because of the immense amount of energy which can be dissipated over short distances.

By employing the natural boron content of the crystal $\text{NaMgB}_3\text{Si}_6\text{O}_{27}(\text{OH})_4$ (tourmaline) as the fissionable source, amorphism is produced after exposure to 7.8×10^{19} thermal neutrons/cm². The reaction which produces the heavy charged

particle is as follows: $\text{B}^{10}(n,\alpha)\text{Li}^7 + 2.4 \text{ Mev}$, natural cross section 750 barns. The total energy as given is divided between the alpha particle and the recoil nuclei, and the very large cross section makes the reaction attractive for producing damaging effects.

Similarly, Al_2O_3 (sapphire) single crystals containing natural lithium (0.15% Li_2O) as a substitutional replacement for aluminum were exposed to an integrated neutron flux of 1.8×10^{20} neutrons/cm² and were subjected to fast-neutron bombardment as well as charged-particle irradiation due to the following reaction for thermal neutrons: $\text{Li}^6(n,\alpha)\text{H}^3 + 4.8 \text{ Mev}$, natural cross section 70 barns. X-ray transmission patterns of this crystal, using unfiltered and monochromatic radiation, are shown in Fig. 135. It is seen that the Laue reflections remain sharp and intense but that a diffuse scattering pattern containing a symmetry related to the crystal diffraction symmetry is produced as a result of irradiation. Small distortions of the lattice, amounting to +0.20% in a_0 and +0.21% in c_0 , were measured. Unfortunately, in this case, the effects of fast neutrons and heavy charged particles are superimposed, so that the real contributions of the latter were not determined.

An exceptionally clear case for the differentiation of fast-neutron effects and fission-fragment effects is seen in the case of natural ZrO_2 (baddeleyite). More often than not, natural samples of this oxide contain uranium and thorium impurities in concentrations ranging as high as 1%. Polycrystalline samples of the oxide containing measured concentrations of uranium impurities were measured by the Debye-Scherrer method before and after several irradiations. At

Fig. 134. ZrSiO_4 (Zircon). Precession photographs, zero level ($h0l$) projection; (a) unirradiated, (b) after irradiation with 3.6×10^{20} neutrons/cm², (c) same as (b) after annealing at 1600°C.

the same time synthetic single crystals and powders of pure oxide were exposed to reactor neutrons for prolonged irradiations as well. The results²⁹ of this experiment were that the monoclinic structure of ZrO_2 is stable under fast-neutron bombardments as high as 3.6×10^{20} neutrons/cm² but that the monoclinic structure transforms to the high-temperature face-centered cubic phase upon fission-fragment irradiation. The fission reaction producing this crystal transformation is as follows: $\text{U}^{235}(n,f)$ fission fragments + 160 Mev, natural cross section 3.92

²⁹M. C. Wittels and F. A. Sherrill, *Phys. Rev. Letters* 3, 176 (1959).

barns. Although the cross section for the reaction is small, the amount of energy dissipated by the pair of fission fragments is enormous. By measuring the fraction of transformed material in partially transformed crystals (Fig. 136) it can be determined that the energy dissipated by a pair of fission fragments in ZrO_2 affects 2×10^6 atoms, thereby causing a transformation in a small region $\sim 140 \text{ \AA}$ in diameter. The stability of the crystals when exposed to fast neutrons alone indicates that the transformation mechanism is a "fission spike," whereby a small localized region is heated above the transition temperature and rapidly quenched.

Fig. 135. Al_2O_3 (Sapphire) Containing 0.15% Li_2O . Laue transmission photographs, x-ray beam parallel to c axis; (a) unirradiated, (b) after irradiation with 1.8×10^{20} neutrons/cm², (c) transmission photograph of (b) using monochromatic $\text{Mo } K_\alpha$ radiation.

Fig. 136. ZrO_2 (Baddeleyite). Debye-Scherrer photographs of samples irradiated with fission fragments; (a) unirradiated, (b) after irradiation with 7.66×10^{14} fission fragment pairs/cm³, 5% transformed, (c) after irradiation with 6.67×10^{15} fission fragment pairs/cm³, 50% transformed, (d) after irradiation with 1.07×10^{16} fission fragment pairs/cm³, 80% transformed, (e) after irradiation with 3.39×10^{16} fission fragment pairs/cm³, completely transformed.

Phase Transitions Due to Fast-Neutron Irradiation

The compounds BaTiO_3 , KNbO_3 , and PbTiO_3 are perovskite-type crystals that deviate from ideal cubic symmetry at room temperature and transform at higher temperatures to the cubic phase. When exposed to fast-neutron dosages in excess of 10^{19} neutrons/cm², these crystals transform^{30,31} into the high-temperature cubic modification. The transformation in BaTiO_3 proceeds by the anisotropic growth of the tetragonal axes (Fig. 137). In unirradiated

Fig. 137. Lattice Expansion of BaTiO_3 as a Function of Fast-Neutron Dosage.

BaTiO_3 , at the upper Curie temperature (120°C), thermal atomic motion is sufficient to overcome the weaker restoring force perpendicular to the c axis and the subsequent transformation into the cubic phase. In the irradiated crystal, at a lower temperature (85°C), the internal strains produced by interstitial atoms are probably similarly relieved by a growth in the weaker directions. The annealing behavior of the transformed crystal (Fig. 138) shows the remarkable thermal stability of the irradiated material. After annealing at 1000°C , the crystal is still cubic but with a

³⁰M. C. Wittels and F. A. Sherrill, *J. Appl. Phys.* **28**, 606 (1957).

³¹M. C. Wittels, *Bull. Am. Phys. Soc.* **4**, 285 (1959).

Fig. 138. Lattice Parameter Annealing of Irradiated BaTiO_3 .

lattice parameter equivalent to that of the original tetragonal c axis. After annealing at 1550°C , the crystal is still cubic but the lattice parameter then jumps down to that of the original tetragonal a axis. In effect, the combination of irradiation and annealing results in a transformed crystal with a smaller volume than the original unirradiated crystal. Through the entire irradiation and annealing procedure the single-crystal structure is retained.

The results of fast-neutron irradiation in KNbO_3 and PbTiO_3 are very similar to those for BaTiO_3 , with the exception that the irradiation-induced phase transition is observed at lower dosages (4×10^{19} neutrons/cm²); KNbO_3 is orthorhombic at room temperature but transforms to a tetragonal³² cell at $\sim 228^\circ\text{C}$ and into a cubic structure at $\sim 435^\circ\text{C}$. After irradiation with 4×10^{19} neutrons/cm², the Laue transmission photographs (Fig. 139) show the distortion induced by the bombardment, together with diffuse scattering that was seen from irradiated BaTiO_3 (ref 30). Precession, Weissenberg, and powder patterns confirmed the formation of a perovskite-type crystal as a result of neutron irradiation. Annealing these transformed crystals at 1000°C produced only small lattice parameter shifts, but the cubic crystals retained their perovskite-type symmetry.

³²E. A. Wood, *Acta Cryst.* **4**, 353 (1951).

The compound PbTiO_3 is tetragonal³³ at room temperature and transforms into a perovskite-type cubic structure at $\sim 490^\circ\text{C}$. Figure 140 shows the Laue transmission patterns of a crystal irradiated with 4×10^{19} neutrons/cm². Note the exact identity of the two projections, indicating

³³G. Shirane and S. Hoshino, *J. Phys. Soc. Japan* **6**, 265 (1951).

the higher symmetry. The annealing behavior of irradiated PbTiO_3 is similar to that for KNbO_3 , since the transformed cubic crystal is thermally stable and retains its cubic symmetry.

Macroscopic Integrity of Neutron-Irradiated Crystals

None of the crystals discussed in this review suffered any obvious macroscopic damage such as

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Fig. 139. KNbO_3 . Laue transmission photographs, x-ray beam parallel to c axis; (a) unirradiated, (b) after irradiation with 4×10^{19} neutrons/cm².

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Fig. 140. PbTiO_3 . Laue transmission photographs, both after irradiation with 4×10^{19} neutrons/cm²; (a) x-ray beam parallel to tetragonal c axis, (b) x-ray beam parallel to tetragonal a axis.

cracks, bubbles, or flaws as a result of fast-neutron irradiation. Although volume changes ranging from a few tenths of a per cent to more than 14% were produced it is notable that natural crystal faces were left unperturbed. An interesting if somewhat unrelated effect is the strain pattern induced in irradiated and annealed Brazilian twinned quartz (Fig. 141). This twinned crystal was irradiated with 7.6×10^{19} neutrons/cm², still retaining some long-range order, and then annealed at 950°C for 30 min. Note the development of slotted holes within the twin bands and the associated strains which are visible in polarized light.

Discussion

The structural effects of irradiation upon non-metallic crystals are highly variable, as determined by x-ray diffraction techniques. Some crystals become amorphous after bombardment with fast-neutron fluxes as little as 1.6×10^{20} neutrons/cm² (quartz), while others display a high degree of perfection even after irradiation dosages as high as 8×10^{20} . There are no clear-cut answers to explain these wide differences in stability, but it would appear that the type of binding, atomic packing in the lattice, and crystal structure all play a role in the ultimate stability of a crystal under fast-neutron bombardment.

Those crystals which contain more ionic binding appear to be more resistant to radiation effects, but this does not seem to be a useful general rule. It should be pointed out that this possible explanation was first given by Goldschmidt and Thomassen³⁴ in their study of the so-called metamict crystals.

If displacements are produced in an anisotropic crystal, however, the effects which are observed are invariably anisotropic as well. As a result, lattice parameter shifts in such crystals are anisotropic, and bombardment-induced defects are often strategically trapped, thus restricting normal thermal atomic motion. From these effects one finds irradiation-induced phase transitions to high-temperature forms and a very high thermal stability for the transformed crystals, as well.

In addition to the effects due to fast neutrons, a few examples of effects due to charged-particle irradiations employing thermal-neutron reactions with the B¹⁰ nucleus and the Li⁶ nucleus have been investigated. Another phase transition was found to be due to the energy dissipated by fission fragments in a crystal lattice (ZrO₂),

³⁴V. M. Goldschmidt and L. Thomassen, *Skripter Norske Videnskaps-Akad. Oslo. I. Mat.-Naturv. Kl.* 1, No. 5, 58 (1924).

Fig. 141. Quartz Crystal. Brazilian twins viewed parallel to *c* axis in polarized light; irradiated with 7.6×10^{19} neutrons/cm² and annealed for 30 min at 950°C.

and again the transition was to a more symmetrical high-temperature form. From this analysis it was found that the energy dissipated by a single fission fragment in ZrO_2 affected $\sim 10^6$ atoms through what is believed to be a "fission spike" mechanism.

The displacement of atoms in nonmetallic crystals by knock-on collisions produces interstitials, vacancies, and complex aggregates. When the concentrations of these defects are sufficiently high, x-ray reflections are broadened, lattice parameters are distended, and, often, a diffuse x-ray scattering appears in diffraction patterns of irradiated crystals. It is interesting to note that crystals which suffer volume changes as high as several per cent continue to retain macroscopic integrity.

FISSION FRAGMENT DAMAGE IN ZIRCONIA

M. C. Wittels

F. A. Sherrill

The effect of fissionable impurities on the structural integrity of ZrO_2 in a thermal-neutron environment was studied. The following has been published in the open literature:

Fission Fragment Damage in Zirconia.³⁵ M. C. Wittels and F. A. Sherrill. — Polycrystalline samples of ZrO_2 containing known concentrations of fissionable impurities were subjected to thermal-neutron dosages at irradiation levels capable of producing partial transformation from the monoclinic to the cubic structure. By determining the fraction of transformed material in partially transformed crystals it can be estimated that $\sim 2 \times 10^6$ atoms are affected by each fission-fragment pair through a "fission spike" mechanism. Contrary to earlier beliefs, it was also determined that pure monoclinic ZrO_2 is stable under fast-neutron dosages as high as 3.6×10^{20} nvt.

³⁵M. C. Wittels and F. A. Sherrill, *Phys. Rev. Letters* 3, 176 (1959).

MAGNETIC SUSCEPTIBILITY OF POTASSIUM RHENIUM CHLORIDE

E. Sonder

Measurement of the magnetic susceptibility of K_2ReCl_6 was motivated by the discovery of a number of anomalies in the specific heat of that compound.³⁶ Specific heat peaks were observed at 76, 103, and 111°K, and it seemed probable that some of these were due to magnetic changes in the material.

A small amount of powdered K_2ReCl_6 was placed in a cavity in a small ($0.5 \times 0.5 \times 2$ cm) piece of fused silica and measured in that container. Since the magnetic susceptibility of fused silica is independent of temperature (actual measurement of the empty container confirmed that χ was temperature-independent except for a very small paramagnetic term below 10°K, for which a correction of about 1% was made), it was possible to separate the paramagnetic component of the K_2ReCl_6 from the temperature-independent diamagnetic contributions of the silica and the rhenium compound. Normalizing in the vicinity of room temperature to the known³⁷ expression $\chi = 3.5 \times 10^{-3}/(T + 57)$ yielded the curves shown in Fig. 142.

The reversal in the temperature dependence of χ near 15°K was unexpected, indicating that an antiferromagnetic phase might be present at low temperatures. However, the temperature of the reversal is nowhere near the temperature of the specific heat anomalies. On the other hand, a closer look at the curve of $1/\chi_p$ vs T does indicate that deviations from the Curie-Weiss law become apparent at temperatures much higher than the 15°K at which the reversal of the slope occurs.

³⁶R. H. Busey, H. H. Dearman, and Q. V. Larson, *Chem. Semiann. Prog. Rep.* June 20, 1956, ORNL-2159, p 11-16.

³⁷C. M. Nelson, *Magnetochemistry of Technetium and Rhenium*, Doctoral Thesis, University of Tennessee (1952).

Fig. 142. The Paramagnetic Component of the Susceptibility and Its Reciprocal Plotted as a Function of Temperature.

POLYMERS AND CERAMICS

O. Sisman

W. W. Parkinson, Jr.

C. D. Bopp

A major objective of the investigation of the effects of radiation on organic polymers and ceramics is to obtain information on which to base the selection of nonmetallic materials for use in reactors and for the prediction of service lifetimes of these materials in reactor uses. The studies are also directed toward providing fundamental information about the nature of the changes produced by radiation.

The current investigations of organic polymers are aimed at determining changes in molecular structure, measurement of the radiation energy required for cross-linking or scission of various polymers, and determining the influence of variables of the radiation field or of the physical state of the polymer. Changes in molecular structure are being studied by infrared spectrometry and by measurement of the gaseous decomposition products. Cross-linking and scission are measured by changes in molecular weight.

The studies of ceramics include changes in physical properties and certain changes in composition, specifically, loss of water. The physical properties which are being measured are elastic modulus, density, hardness, thermal conductivity, and specific heat. These properties provide information about changes in structure as well as engineering information.

In the mixed radiation and energetic-particle field of a nuclear reactor, the energy imparted to an irradiated material depends on the energy spectrum of the neutrons and gamma radiation and on the composition of the irradiated material. Rather than measure the exact energy spectra it has been found that satisfactory approximations of the energy deposited in sample materials of known composition can be obtained from measurements of the energy deposition in selected elements by the components of the radiation field. Such a monitoring program is of prime importance in the study of radiation effects on nonmetallic materials, since energy absorbed both from the gamma radiation and from the energetic neutrons produces large changes in the materials.

During the period of this report, most of the personnel working in this program have been involved in writing chapters for two books. As a result, some of the problems discussed in previous

reports have been inactive during the past year. One of the books is an AEC-sponsored project, *Radiation Effects in Organic Materials*; the other deals with the uses of various sources of radiation in the study of radiation effects, to be published by Pergamon Press under the editorship of A. Charlesby.

POSTIRRADIATION MOLECULAR WEIGHT CHANGES IN POLYMETHYL METHACRYLATE

W. W. Parkinson D. Binder W. K. Kirkland

An investigation of the radiation-induced scission of polymethyl methacrylate revealed that the molecular weight of this material continued to change after removal from the radiation field. The post-irradiation change in a physical property is of importance in the measurement of radiation effects, although it has been known for several years that free radicals and perhaps other reactive species are trapped in solid polymers during irradiation.^{1,2}

Samples of polymethyl methacrylate were sealed in Pyrex glass tubes after evacuation to 2μ for 24 or more hours. The samples were then irradiated in a Co^{60} source and stored at room temperature in their evacuated capsules for periods up to 500 hr. At the end of the storage period, the capsule was opened and the sample was dissolved in chloroform for viscosity measurements. The solution viscosities were converted to molecular weights by the relations:

$$[\eta] = 4.8 \times 10^{-5} M_v^{0.8} ,$$

$$M_v = 1.9 M_n ,$$

where $[\eta]$ is the intrinsic viscosity obtained by extrapolation to zero concentration, M_v is the viscosity average molecular weight, and M_n is the number average molecular weight.

Three series of specimens were irradiated initially. Two were irradiated at an intensity of

¹R. J. Abraham *et al.*, *Trans. Faraday Soc.* 54, 1133 (1958).

²L. A. Wall and D. W. Brown, *J. Research Natl. Bur. Standards* 57, 131 (1956).

about 10^7 rads/hr to total doses of 1.36 and 0.82×10^6 rads, respectively. The third series was irradiated at 10^6 rads/hr to 1.35×10^6 rads. For convenience in evaluating the radiation and aging effects, the data were plotted in terms of the number of molecules per gram, inversely proportional to molecular weight, since each radiation-induced scission produces one new molecule. Figure 143 shows the increase in number of molecules per gram with postirradiation storage time.

To investigate the possibility that dissolved oxygen in the specimens was giving rise to the postirradiation instability through the formation of an unstable oxidation product, another series of specimens was prepared. These specimens were evacuated at 140°C for 24 hr at 2μ before sealing the sample tubes prior to irradiation. This series was irradiated at 10^6 rads/hr to a dose of 1.35×10^6 rads. The specimens were stored, following irradiation, for suitable periods at room temperature, as before. The number of molecules per gram varied as a function of time in these specimens (Fig. 144) in a manner which was approximately the same as that of the specimens outgassed at room temperature.

Fig. 143. Scission of Polymethyl Methacrylate Following Irradiation. Samples evacuated at room temperature.

Fig. 144. Scission of Heat-Treated Polymethyl Methacrylate Following Irradiation. Samples irradiated to 1.35×10^6 rads at 10^6 rads/hr.

In an effort to deactivate the reactive species, two additional series of specimens were irradiated at room temperature and then heated to 80°C for 1 hr. These specimens also received a dose of 1.35×10^6 rads at a rate of 10^6 rads/hr. One of these series had been evacuated at room temperature, the other at 140°C for 24 hr, during encapsulation prior to irradiation. After the postirradiation heat treatment both series were aged at room temperature in their evacuated irradiation capsules. As in the earlier series, capsules were opened at intervals for dissolution of the samples and for viscosity measurements. As shown in Fig. 144, the postirradiation heating produced about the same increase in the number of molecules per gram (decrease in average molecular weight) as had aging at room temperature for 500 hr. Subsequent to the heat treatment, a slow decrease in number of molecules per gram (increase in molecular weight) was observed, apparently from a recombination or polymerization reaction.

The experimental data were treated analytically, according to equations derived from two possible reaction mechanisms. The first possible mechanism was that of the conventional thermal depolymerization chain reaction. Rate constants and activation energies available from the literature³

³N. Grassie, *Chemistry of High Polymer Degradation Processes*, p 40, Interscience Publishers, Inc., New York, 1956.

were used to calculate the number of molecules as a function of time. The results were considerably higher than the experimental values, possibly because the measured values represented the number of molecules of average molecular weight, while the published reaction rate constants represent the production of the much smaller monomer molecules.

The second possible mechanism examined was slow inactivation of the free radicals during storage, with immediate bimolecular coupling of any remaining radicals at the instant of dissolution for viscosity measurements. The application of equations derived from these reactions to the experimental data leads to concentrations of free radicals and reaction rate constants differing by orders of magnitude from published values.

For the purposes of practical testing, it may be concluded that heating to 80°C for 1 hr, followed by 24 hr of storage at room temperature, will give molecular weights within 5% of that after 500 hr of aging at room temperature.

INFLUENCE OF THE PHYSICAL PROPERTIES OF POLYMERS ON THE EFFECTS OF RADIATION

W. W. Parkinson J. E. White⁴
W. K. Kirkland

In the previous report⁵ differences in the radiation energy required for cross-linking in oriented and random samples of polystyrene were described. Because of the method of preparation, there were differences in the thickness and perhaps in oxygen content of the specimens, in addition to the differences in molecular orientation. Further experiments on randomized samples have been performed to determine the effect of thickness and heating in air on the behavior under irradiation.

The thicknesses of the oriented and random specimens in the earlier work were 0.010 and 0.080 in., respectively. Randomized specimens of these thicknesses have been irradiated for two irradiation doses. The thickness of the specimens appears to influence the energy required for cross-linking, with the thinner specimens requiring less energy per cross link. This thickness effect

is in the direction to contribute to the difference in cross-linking energy observed earlier⁵ between the thin, oriented specimens and the thicker random specimens.

The magnitude of the thickness effect at the higher doses is adequate to account for the difference observed between oriented and random specimens. At lower doses, however, the difference in cross-linking energy for oriented and random specimens appears to be real and to exceed the effect of differences in thickness.

Specimens are now being prepared in various thicknesses and with different heat treatments to determine whether the thickness effect is caused by reactive material generated during irradiation or during the preirradiation heat treatment. Exposure of the specimens to air after irradiation has indicated that thickness effects are not due to postirradiation oxidation of the thin samples.

RADIATION STABILITY OF DEUTERATED BASIC BERYLLIUM ACETATE COMPLEX

W. W. Parkinson

Beryllium forms an unusual series of complex derivatives with monobasic carboxylic acids. These complexes are volatile, nonionized, soluble in hydrocarbons but insoluble in water. The best known of these complexes is basic beryllium acetate which has the formula $\text{Be}_4\text{O}(\text{OCOCH}_3)_6$. This compound melts at 285–286°C and boils without decomposition at 330°C.

The completely deuterated compound is similar in properties to the hydrogen compound. The stability of the complex and the nuclear properties of the elements in the deuterated compound have led to the suggestion that it be used as a moderator in nuclear reactors.⁶ One of the decisive criteria in such an application is the stability of the material in the neutron and gamma-radiation field of a nuclear reactor. The gas evolution and weight loss of the deuterated compound resulting from irradiation in a Co^{60} source have been measured by Rollier and Maxia.⁷ A series of irradiations has been carried out in the ORNL Graphite Reactor to determine the effect of the

⁴Summer Research Participant, Lafayette College, Easton, Pa.

⁵W. W. Parkinson *et al.*, *Solid State Ann. Prog. Rep.* Aug. 31, 1958, ORNL-2614, p 117.

⁶M. A. Rollier, *Second U.N. Conf. on Atomic Energy*, 1958, paper 2325.

⁷M. A. Rollier and V. Maxia, *Nucleonics* 17(5), 162 (1959).

combined neutron and photon bombardment encountered in reactor service. Gas evolution was measured as an indication of decomposition, and the melting point and x-ray diffraction pattern were determined in order to show changes in the residual solid.

The material was in the form of a white powder, supplied by M. A. Rollier, University of Cagliari, Sardinia, Italy. The powder was baked at 80°C for 3 hr under about 30 mm Hg pressure to remove occluded gas. Samples were then weighed into quartz tubes of 10 mm diameter which had a standard-taper male joint containing a breakoff-tip closure at one end. Aluminum foil was tamped into the irradiation tube to act as a heat reflector. The tube was evacuated to 2μ Hg pressure for 24 or more hours and sealed. The irradiation tube was then wrapped in aluminum foil along with a cobalt monitor foil (3–5 mg) and inserted in a watertight aluminum can.

Irradiations were carried out in water-cooled Hole 19 in the Graphite Reactor for periods up to 400 hr. The thermal-neutron flux in this facility is 6×10^{11} neutrons·cm⁻²·sec⁻¹. The fast-neutron flux is about one-tenth of this, while the gamma radiation intensity is about 200 r/sec. The cooling water temperature is 15–20°C.

After irradiation, the irradiation tubes were connected to a gas collection apparatus consisting of a nitrogen-cooled trap, a Toepler pump, three bulbs of known volume, and a mercury manometer. The gas evolved by radiation was then transferred and measured in the calibrated bulbs, with the trap at liquid-nitrogen temperatures. The liquid nitrogen was removed from the trap, and the gases condensable at -190°C were measured. The gas evolved per gram of sample is plotted in Fig. 145 vs reactor exposure, expressed in terms of energy deposited per gram of sample by both neutrons and gamma radiation and in terms of integrated thermal-neutron flux.

The melting points of the specimens were determined in a copper-block apparatus which held several capillary sample tubes in contact with a thermometer bulb. The copper block was electrically heated, at 2–3 deg/min in the melting range, and the sample tubes were observed through a viewing port. The melting points are shown in Fig. 146, as a function of radiation dose.

Exposures are expressed in terms of energy absorbed per gram of sample, based on calorimetric

Fig. 145. Gas Evolved During Irradiation of $\text{Be}_4\text{O}(\text{OCOCD}_3)_6$.

Fig. 146. Melting Points of Irradiated $\text{Be}_4\text{O}(\text{OCOCD}_3)_6$.

measurements in Hole 19, by Bopp.⁸ These measurements yielded the energy imparted to the elements hydrogen and carbon for a known thermal-neutron flux. The values for these elements were converted to the energy deposited in deuterated basic beryllium acetate by using the ratio of the energy deposited in deuterium to that deposited in hydrogen and the ratio of the energy deposited in beryllium and oxygen to that deposited in carbon. These ratios were calculated

⁸C. D. Bopp, this report.

from integrals of the neutron spectrum and the neutron scattering cross section reported by Richardson, Allen, and Boyle.⁹

The x-ray diffraction patterns of irradiated and unirradiated samples were obtained by conventional powder techniques. No changes were noted after irradiation. Very faint lines from BeO appeared in both irradiated and unirradiated samples. The minimum change in BeO content which could have been detected was probably 3–5% of the sample weight.

The gas evolution measurements gave a G value (yield in molecules per 100 ev) of 0.52 ± 0.05 for total gas. The G value for gases uncondensed at liquid-nitrogen temperatures was 0.41 ± 0.04 . The gas evolved was not analyzed, but the mixture would be expected to consist of H_2 , CO , CH_4 , CO_2 , and H_2O , with the latter two making up the fraction condensed in the trap at liquid-nitrogen temperature. These G values are about twice the values reported for smaller gamma irradiations.⁷

Although no change was noted in the x-ray diffraction pattern of the samples after irradiation, the change in melting point is an indication that the composition of the residual material has changed in some respect. The sensitivity of the x-ray determination was inadequate to detect the change in BeO content if it is assumed that three molecules of gas are evolved for one molecule of BeO produced.

RADIATION STABILITY OF CERAMIC MATERIALS

C. D. Bopp R. L. Towns

The limit on the temperature for the serviceability of asbestos is ordinarily set by the loss of chemically combined water, since the strength is greatly decreased after the water is driven off. In order to investigate the effect of irradiation on the thermal stability, samples of Cassiar, Thetford, crocidolite, and amosite asbestos were irradiated in the isotope stringer of the ORR to an integrated thermal flux of 2×10^{20} nvt. (Roughly, the epithermal flux is of the same

order.) It is planned to measure the epithermal flux at this position with threshold detectors. The samples were all irradiated in the same quartz capsule, which was evacuated and then filled with helium.

The weight change was measured after heating in vacuum to 1000°C , at about 200°C/hr . In the present work, the best sensitivity was attained by weighing the sample and its container before and after heating. The weight of the quartz tube which was used as a sample container remained constant within 0.05%. The weight change was also followed during heating by measuring the change in the deflection of a spring, according to a method which has been described,¹⁰ except that a Chromel spring was used and the deflection was followed with a differential transformer.¹¹ The sensitivity was limited by a false signal due to the change in furnace alignment on heating. It is planned to remove this defect by increasing the clearance in order that the furnace will not contact the other apparatus.

The preirradiation weight loss for the Cassiar and Thetford chrysotile was 14%, corresponding to the water content.¹² Irradiation did not change the weight loss for the Cassiar asbestos, but the weight loss for the Thetford was increased to 20%. The difference in behavior may be associated with the carbonate content, since this may vary from zero to several per cent for different kinds of chrysotile. The temperature for the loss of water was not changed from $600 \pm 50^\circ\text{C}$ by the irradiation exposure, for either of the two kinds of chrysotile. The additional weight loss for Thetford asbestos occurred in the range from 200 to 300°C . The weight loss of crocidolite asbestos changed from a preirradiation value of 2% to a postirradiation value of 4%. It was not determined in what temperature range the additional loss occurred. The weight loss of amosite asbestos was less than 1%, both before and after irradiation. It is planned to extend this study to longer exposures.

¹⁰S. L. Madorsky, *J. Polymer Sci.* 9, 133 (1952).

¹¹C. Campbell and S. Gordon, *Anal. Chem.* 29, 298 (1957).

¹²C. Z. Carroll-Porczynski, *Asbestos*, The Textile Institute, Manchester, Eng., 1956.

⁹D. M. Richardson, A. O. Allen, and J. W. Boyle, *U.N. Conf. on Uses of Atomic Energy* 1955, paper 575.

ENERGY ABSORPTION IN A REACTOR

C. D. Bopp D. Binder R. L. Towns

Calorimetric Measurements

The energy absorption in a mixed radiation field may be separated into the components from fast neutrons and from gamma radiation by measurement of the energy absorption in graphite and in a hydrogen-containing material.¹³ The values determined are listed in Table 20. The values for Hole 51 were determined with the modified calorimeter, which is described below. The values for Hole 19 are the same values reported previously¹³ except that the correction to thin specimens and the correction to account for the effect of the thermal-neutron reaction with N^{14} have been applied. The lower percentage of energy absorption from gamma radiation in Hole 19 as compared to that in Hole 51 results from the shielding of the fission gamma radiation by the graphite. The channel in the graphite for Hole 51 is larger than the channel for Hole 19.

The calorimeter described previously was modified for use at higher temperature and higher flux intensity by omitting the Styrofoam supports and insulators and by supporting the inner cylinders with wires (Fig. 147). As before, the temperature difference is measured across the air gap between a heat shield surrounding the inner cylinder and the outer aluminum can. The copper foil employed previously for the heat shield was

replaced with aluminum in order to reduce the energy absorption from the decay products of the thermal-neutron capture reaction. Small fluctuations in the temperature of the cooling water which surrounded the outer can in the previous design necessitated averaging readings taken over long periods. In the present design the outer can was made thinner (20 mils) in order to eliminate the need for cooling water, and no fluctuation in the reading was observed after the steady state was reached. The size of the inner cylinder ($\frac{1}{2}$ in. in diameter and $\frac{5}{8}$ in. long) represents a compromise. A smaller size would give less self-shielding of the neutron and gamma fluxes;

Fig. 147. Schematic of Neutron and Gamma-Radiation Calorimeter.

¹³C. D. Bopp, O. Sisman, and R. L. Towns, *Solid State Ann. Prog. Rep.* Aug. 31, 1958, ORNL-2614, p 121.

Table 20. Energy Absorption in the Graphite Reactor at 3500 kw Power

Position	Element	Energy Absorption ($\text{ev}\cdot\text{g}^{-1}\cdot\text{sec}^{-1}$)	
		From Fast Neutrons	From Gamma Radiation
		$\times 10^{17}$	$\times 10^{17}$
In Hole 51, in center of converter	Hydrogen	6.1 ± 0.3	0.70
	Carbon	0.08	0.35 ± 0.02
In Hole 51, outside the converter, 12 in. from center	Hydrogen	1.6 ± 0.2	0.20
	Carbon	0.02	0.10 ± 0.01
In Hole 19, $5\frac{1}{2}$ ft from center toward north face	Hydrogen	1.5 ± 0.2	0.11
	Carbon	0.02	0.06 ± 0.01

however, the energy absorption from the decay products of thermal-neutron capture by the support wires, heat shield, thermocouple, and heater would constitute a larger fraction of the total absorption.

Calibration of the temperature difference in terms of energy absorption was obtained in a Co^{60} source in which the radiation field was known from ceric sulfate dosimetry. Electric heaters in the inner cylinders provided a second means of calibration. Comparison of the two methods showed that, to produce a given temperature difference, about 10% more electrical energy was required than energy absorbed from the radiation field. This condition results because more energy is lost by convection currents at the heater lead wires when the heater is hot. This effect was not significant in the previous design, since the heater lead wires were insulated with Styrofoam. Even though the electrical method does not give an absolute calibration, it is useful in testing the linearity and in testing the constancy of the thermal resistance.

Energy absorption from decay products from thermal-neutron reactions in the inner cylinder is appreciable only for the $\text{N}^{14}(n,p)$ reaction in the nylon cylinder. (Nylon, which was employed as a hydrogen-containing material, has the disadvantage of having a 12% nitrogen content, but the advantages of having a high melting point and a high hydrogen content.) In accord with the difference in the energy absorption from fast neutrons to thermal flux ratios for the two positions, the energy from the $\text{N}^{14}(n,p)$ reaction with thermal neutrons is 4% of the energy absorption from fast neutrons in the converter in Hole 51 and 25% in Hole 19.

The number of first collisions with fast neutrons in a thick specimen is decreased by self-shielding.¹⁴ Second collisions partly compensate for the decrease in first collisions. The inner nylon cylinder was approximated as a sphere of 0.8 cm radius, and a uniform source of neutrons from first collisions was taken for the calculation of second collisions. For a fission spectrum, 6% less energy is absorbed from fast neutrons than for a thin specimen; for the moderated spectrum in Hole 19, 13% less.

It is conceivable that the electron flux from the decay of Al^{28} in the outer can may contribute to the energy absorption in the inner cylinder. It is difficult to calculate this effect since a

spectrum of electron energies is involved and both elastic and inelastic scattering are important. In order to test for an electron contribution, $\frac{1}{8}$ -in.-thick sheets of methyl methacrylate were irradiated bare and sandwiched between $\frac{3}{32}$ - and $\frac{3}{16}$ -in.-thick graphite sheets. The energy absorbed was determined by solution viscosity.¹⁵ The reduction by the shielding was approximately linear with graphite thickness and was $(6 \pm 2)\%$ for $\frac{3}{16}$ -in.-thick graphite. The reduction to be expected only from attenuation of the gamma and neutron radiation is $(5 \pm 2)\%$. It follows that the contribution from Al^{28} electrons for the sheets is less than 5% of the total energy absorption, or 10% of the gamma component. In order to relate the effects for the sheet and for the cylinder used in the calorimeter, it is necessary to know the absorption coefficient. The coefficient which gives the reduction in the number of electrons¹⁶ represents a lower limit, since it gives no measure of the softening of the spectrum, and it gives an upper limit for the effect in the cylinder as compared with the effect in the sheet. On this basis, the effect in the calorimeter is not greater than half that for the sheet, or the electron component is from 0 to 5% of the gamma component for Hole 19.

The calculation of the neutron component from the measurements for graphite and nylon is affected by the size of the electron component. For an electron component which is 5% of the gamma component, the calculation gives a neutron component 10% greater than if the electron component is negligible. This represents the uncertainty by which the results listed in Table 21 may be low for Hole 19 and for Hole 51 outside the converter. There is no effect inside the converter in Hole 51 since the energy absorption to thermal flux ratio is several fold greater. Changes in the design of the calorimeter which would reduce interaction with thermal neutrons are the use of graphite in place of aluminum for the outer can and the substitution of a hydrogen-containing material which does not contain nitrogen for nylon.

¹⁴A. Weinberg and E. Wigner, *The Physical Theory of Neutron Chain Reactions*, p 714, Eq. 20.19, Univ. of Chicago Press, Chicago, 1958.

¹⁵D. Binder, W. W. Parkinson, and W. K. Kirkland, *Solid State Ann. Prog. Rep. Aug. 31, 1957*, ORNL-2413, p 100.

¹⁶R. G. Baker and L. Katz, *Nucleonics* 11(2), 14 (1953).

Table 21. Neutron Flux in Holes 19 and 51 of the Graphite Reactor

Hole	Position	Neutron Flux (neutrons·cm ⁻² ·sec ⁻¹)			
		ϕ_0	$\phi(>0.6 \text{ Mev})$	$\phi(>1.5 \text{ Mev})$	$\phi(>3.0 \text{ Mev})$
		$\times 10^{11}$	$\times 10^{11}$	$\times 10^{11}$	$\times 10^{11}$
19	5.5 ft from center	0.33 $\pm$ 0.05	1.0	0.26 $\pm$ 0.04	0.08
51	Center of converter	0.30	3.2	1.75	
51	12 in. from center of converter	0.30	1.09	0.51	

Neutron Flux Measurements

The energy absorption from fast neutrons may be calculated from foil activation data, from which a neutron flux spectrum is derived. The accuracy of the calculation is dependent on the effect of errors in the construction of the neutron flux spectrum. As a test of this method, the values derived from foil activation data were compared to the calorimetric measurements made in Holes 19 and 51. The input data are shown in Table 21.

The flux per $\ln E$ interval in an assumed $1/E$ spectrum is tabulated as ϕ_0 . This spectrum is assumed to extend to 0.6 Mev and was measured outside the uranium converter in Hole 51 by the cadmium ratios for several resonance reactions. The value at the center of the converter is assumed to be the same. The value of ϕ_0 in Hole 19 is estimated from the thermal flux and cadmium ratios in similar holes in the pile.

The flux greater than 0.6 Mev [$\phi(>0.6 \text{ Mev})$] was measured by the Np^{237} fission reaction,¹⁷ [$\phi(>1.5 \text{ Mev})$] by the U^{238} fission reaction, [$\phi(>3.0 \text{ Mev})$] by the $\text{S}^{32}(n,p)$ reaction. The fluxes in Hole 51 are given for the center of the converter and 12 in. from the center, or outside the converter. Subtracting the fluxes outside from those at the center, the remaining values of [$\phi(>0.6 \text{ Mev})$] and [$\phi(>1.5 \text{ Mev})$] have a ratio within 7% of the ratio for a fission spectrum. It was therefore assumed that the converter added a fission spectrum to the spectrum outside the converter.

The spectrum outside the converter, as well as the spectrum in Hole 19, was approximated by assuming a $1/E$ variation below 0.6 Mev. Above 0.6 Mev the spectrum was divided into blocks between 0.6 and 1.5 Mev, 1.5 and 3.0 Mev (or above 1.5 Mev), with average energies of 1.0 and 2.3 Mev. The spectrum inside the converter is then the sum of a well-known fission component and an approximate block spectrum. The results of the calculation of the energy absorbed in hydrogen in Holes 19 and 51 for these spectra are shown in Table 22 along with the calorimetric values.

The two methods agree within experimental error at the three positions in the reactor, but the test is sensitive only at the center of the converter. At the other positions, the errors preclude any conclusion about the calculation of the energy absorbed if foil activation data are used.

Table 22. Comparison of Energy Absorption in Hydrogen as Calculated from Neutron Flux and Calorimetric Measurements

Hole	Position	Energy Absorbed in Hydrogen (ev·g ⁻¹ ·sec ⁻¹)	
		Neutron Flux	Calorimeter
		$\times 10^{17}$	$\times 10^{17}$
51	Center of converter	5.8 $\pm$ 0.4	6.1 $\pm$ 0.3
51	12 in. from center of converter	1.8 $\pm$ 0.1	1.6 $\pm$ 0.2
19	5.5 ft from center	1.9 $\pm$ 0.2	1.5 $\pm$ 0.2

¹⁷D. Binder, *Solid State Ann. Prog. Rep.* Aug. 31, 1957, ORNL-2413, p 122.

RELATIVE EFFICIENCIES OF NEUTRONS AND GAMMA RAYS IN POLYMER IRRADIATION EFFECTS

D. Binder

W. K. Kirkland

R. L. Towns

Polymers have been irradiated in a reactor and in a cobalt gamma-ray source to determine the relative efficiencies of fast neutrons and gamma rays in producing irradiation effects. The results are compared to the heat absorbed, as measured by calorimetry, in order to determine whether neutrons or gamma rays are more efficient. The significant index for the fast-neutron effect on polymers is assumed to be the hydrogen content.

In the present work the irradiation effects were studied at the same position in Hole 19 as the calorimetric measurement.¹ The previous assumption² of symmetry relative to the center of the hole was found to be incorrect.

In Table 23 the polymer effects and the calorimetric measurements are listed along with the "gamma equivalents," or the cobalt gamma-ray intensity equivalent to the reactor. The gamma equivalent is made up, in general, of two components, one from the hydrogenous fraction of the substance and one from the nonhydrogenous fraction. The nonhydrogenous fraction absorbs energy mostly from gamma rays, and the hydrogenous component mostly from neutrons. The agreement between the

heat absorbed in graphite and the Teflon density increase indicates that the Teflon effect is caused mainly by gamma rays.

To separate the hydrogen component from the gamma equivalent, the nonhydrogenous component must be subtracted. The latter is determined by multiplying the gamma equivalent for the heat absorbed in graphite by the weight fraction that is not hydrogenous, for each substance. This procedure determines the results listed under "hydrogen component" except for a correction for the $N^{14}(n,p)C^{14}$ reaction in the nylon gassing reaction. The corresponding correction in the heat absorbed in nylon was canceled by another effect.²

The final column in the table, the "hydrogen sensitivity," is the hydrogen component divided by the weight fraction of hydrogen. For the calorimetric measurement, it is the gamma-ray intensity that would produce the same heat in hydrogen as the reactor, or approximately the gamma intensity equivalent to the reactor neutron intensity for pure hydrogen. The two cleavage reactions show a hydrogen sensitivity about half that indicated by calorimetry, and the gassing reactions show greater sensitivities. This indicates that the cleavage reactions have a lower efficiency for fast neutrons than for gamma rays, and that the gassing reactions have a higher efficiency.

¹C. D. Bopp *et al.*, this report.

²D. Binder, W. K. Kirkland, and R. L. Towns, *Solid State Ann. Prog. Rep. Aug. 31, 1958*, ORNL-2614, p 115.

Table 23. Hydrogen Sensitivities for Polymer Effects vs Calorimetric Result

Substance	Reaction	Gamma Equivalent (r/hr)	Hydrogen Component (r/hr)	Hydrogen Sensitivity (r/hr)
		$\times 10^6$	$\times 10^6$	$\times 10^6$
Teflon	Density increase	0.45		
Lucite	Viscosity decrease	0.86	0.42	5.3
Polyisobutylene	Viscosity decrease	1.05	0.64	4.5
Graphite	Heat absorbed	0.48		
Nylon	Heat absorbed	1.38	0.95	9.8
Allyl diglycol carbonate	Gassing	1.6 ± 0.2	1.2 ± 0.2	18 ± 3
Nylon	Gassing	2.4	1.8	19
Polyethylene	Gassing	2.3 ± 0.3	1.9 ± 0.3	13 ± 2

EVALUATION OF THE ORNL GRAPHITE REACTOR

M. C. Wittels

Stored energy measurements were made on samples of moderator graphite from the ORNL Graphite Reactor for purposes of determining whether an annealing operation should be performed. This work has been published, and an abstract appears below:

Evaluation of the ORNL Graphite Reactor.¹ M. C. Wittels. — Measurements were conducted at several laboratories, and each of the laboratories made different types of stored energy measurements in order that independent analyses would be available. The samples were cored from the most severely damaged

region of the graphite moderator for the purpose of determining the most serious situation that exists. Favorable agreement between the different kinds of measurements was obtained, and it was established that the stored energy content was at a reasonably safe level. It was shown that the growth of stored energy in ORNL Graphite Reactor graphite is considerably retarded as a result of moderately high operating temperatures, particularly during the summer months.

¹M. C. Wittels, *US/UK Graphite Conference, Part I*, p 64-81 (Mar. 16, 1959).

CRYOSTAT FOR HOLE 50, ORNL GRAPHITE REACTOR

J. T. Howe

W. E. Busby

R. R. Coltman

The cryostat irradiation facility described previously¹ was installed in Hole 50 of the ORNL Graphite Reactor. A flux of about $3 \times 10^{11} \text{ nv}_f$ and $7 \times 10^{11} \text{ nv}_{th}$ is available at a reactor power of 3400 kw. The ambient temperature is about 320°K.

The cryostat consists of a $1\frac{3}{8}$ -in.-OD aluminum sample tube with a 2-ft-long heat exchanger at the inner end and a 2-ft-long stainless steel heat trap at the outer end. The cryostat readily accommodates samples up to 1 in. in diameter. A curved passage is provided through the Hole 50 shield so that samples may be inserted or withdrawn during pile operation. This curved passage is made of a $1\frac{9}{16}$ -in.-ID telescopic tube on a $24\frac{1}{16}$ -in. center line radius, as shown in Fig. 148. It is this radius which restricts the length of the sample, although, if it were necessary to irradiate a longer sample, the curved passage could be removed and a straight insertion could be made by removing the shield door.

A line diagram of the helium circulating system is shown in Fig. 149. Helium from the cryostat passes through a counterflow heat exchanger in order to cool the helium from the compressor, so that the helium entering the compressor system is at approximately room temperature and the helium entering the liquid-nitrogen tank is at a temperature approaching that of the gas from the cryostat. The amount of cooling required of the liquid nitrogen after steady operation has been attained is, therefore, little more than the heat dissipated in the cryostat. The vaporized nitrogen gas is

utilized to lower the temperature of shields surrounding the nitrogen tank and the counterflow exchanger, so that the entire heat content of the nitrogen from liquid to room temperature is utilized.

The initial test of the cryostat indicates that about 50 liters of liquid nitrogen is required to cool the low-temperature portions to operating temperature. The tank capacity is 50 liters; therefore, 100 liters is required to begin operation. Steady-state operation was maintained with 50 liters/day. A helium flow of 16 scfm, with a heat load of 32 w in the sample chamber, resulted in a helium temperature of 81°K to the cryostat and 88°K from the cryostat, with a sample temperature of 106°K. Full-capacity tests have not been made and will be incorporated with future experiments.

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Fig. 148. Section Through Hole 50 Shield.

¹J. T. Howe, W. E. Busby, and R. R. Coltman, *Solid State Ann. Prog. Rep. Aug. 31, 1958, ORNL-2614*, p 72.

Fig. 149. Helium Circulating System for Hole 50 Cryostat.

HIGH-TEMPERATURE REACTOR FUELS

O. Sisman

J. G. Morgan

The study of the behavior of high-temperature reactor fuels is directed exclusively to the development of fuel materials for gas-cooled reactors. This work is being done in support of the EGCR (Experimental Gas-Cooled Reactor), the first gas-cooled power reactor in this country, and for more advanced gas-cooled reactors to be developed in the future. Materials of current interest are UO_2 , $\text{UO}_2\text{-ThO}_2$, BeO , UC , mixtures of UC and graphite, and to a lesser extent the cermets SiC-Si-UO_2 and $\text{Cr-Al}_2\text{O}_3\text{-UO}_2$.

The fuel element for the EGCR will consist of UO_2 pellets canned in stainless steel, and the most pressing need is for sufficient radiation damage data to guarantee a reasonable life for the first fuel loading. At present, therefore, most of the work in this area is devoted to studying the breakup and movement of UO_2 in various configurations proposed for the EGCR fuel element, and to the study of fission-gas release from UO_2 under varying conditions.

It is anticipated that the mechanism of fission product release will be a continuing fundamental problem for high-temperature fuels. Other fundamental studies that will be undertaken as manpower becomes available are thermal conductivity, thermal expansion, specific heat, Young's modulus, strength, and changes in microstructure.

Much of the work reported here has already been reported in detail in the GCR Quarterly Progress Reports. The discussions presented here have therefore been kept quite brief. The status of certain associated work (hot-cell development, in-pile thermocouple calibration, graphite and coated graphite for fuel element cladding) is also presented.

 UO_2 IRRADIATION STUDIES

M. T. Morgan	J. F. Murdock ¹
M. F. Osborne	J. Gooch

A series of UO_2 irradiations are being conducted in the LITR (Low-Intensity Test Reactor), ORR (Oak Ridge Reactor), GETR (General Electric Testing Reactor), and ETR (Engineering Test

Reactor). With the exception of the LITR, these are prototype or reduced prototype fuel elements proposed for the EGCR (Experimental Gas-Cooled Reactor). The LITR irradiation samples (the only material that has been examined so far) are miniaturized (Fig. 150), and the U^{235} content is increased to produce accelerated burnup. Fission gas sampling was made after irradiation, and stability of the pellets was investigated. A summary of the operating conditions is given in Table 24, and the fission gas release data obtained thus far in Table 25.

It is premature to try to relate the available fission gas release data to existing diffusion equations for fission gas release because of uncertainties in the temperature measurements and the difficulty of interpreting the effect of the temperature gradient between the inside and outside of the fuel pellets. The data show that below central operating temperatures of approximately 2250°F the atom ratio of radioactive gas existing outside the UO_2 pellet (95% theoretical density) to the total existing at the time of sampling is small ($\sim 0.04\%$) and that the variation with temperature is less than 0.005% per 100°F . Only one capsule has been examined that had a central operating temperature higher than 2250°F . This capsule contained pellets of UO_2 of 85% of theoretical density, and the central operating temperature was 2550°F . The fission gas Xe^{133} released was 9% of that existing in the pellet, which is more than 200 times that found for any of the lower-temperature experiments. It seems that this increase in fission gas release can be attributed mostly to temperature rather than to the decrease in density, because another capsule containing pellets of 95% theoretical density evolved 5.5% of the Xe^{133} existing at the time of heating when subjected to a postirradiation heat treatment at 2500°F .

Postirradiation heat treatments of the encapsulated UO_2 in helium at 2100 and 2500°F , caused the evolution of considerable amounts of solid fission products. These data are shown in Table 26. The evolution of Xe^{133} from capsule L-14 was 5.6%, compared with 0.02% before heating.

¹ Summer employee.

Fig. 150. UO_2 Pellets from Capsule UO_2 -1-1 After Irradiation. Hollow pellets, subjected to thermal stress, cracked radially and also, to a lesser extent, transversely. No fine powdering was observed.

Table 24. Operating Conditions for Miniature Capsules Irradiated in the LITR

Experiment Number	Date Installed	Present Status	Irradiation Time (hr)	UO_2 Pellet Theoretical Density (%)	Pellet Enrichment (% U^{235})	Pellet Central Temperature ($^{\circ}\text{F}$)	LITR Core Location
L-1a	10-23-58	Removed 2-25-59	2479	93.2	10	1850	C-47
1b				93.2	10	2100 ^a	C-47
L-2a	2-25-59	Ruptured and removed 4-7-59	726	84.8	20	2480	C-47
2b				84.8	20	2540 ^a	C-47
L-3a	5-19-59	Removed 8-10-59	1820	75	10	<i>b</i>	C-28
3b				75	10		C-28
L-4a	9-30-58	Removed 4-28-59	4194	92.5	10	2350	C-42
4b				92.5	10	2500 ^a	C-42
L-6a	10-23-58	Removed 5-18-59	4208	73.6	10	2250	C-28
6b				74.2	10	2500 ^a	C-28
L-7a	3-17-59	Removed 6-8-59	1750	95.3	10	2160	C-57
7b				95.3	20	2600 ^a	C-57
L-8a	4-28-59	Removed 6-29-59	1324	84.6	20	2660	C-47
8b				85.0	20		C-47

Table 24 (continued)

Experiment Number	Date Installed	Present Status	Irradiation Time (hr)	UO ₂ Pellet Theoretical Density (%)	Pellet Enrichment (% U ²³⁵)	Pellet Central Temperature (°F)	LITR Core Location
L-13a	11-11-58	Removed 6-8-59	4170	92.9	10	2230	C-46
13b				92.9	10	2560 ^a	C-46
L-14a	12-30-58	Removed 3-17-59	1565	94.7	20	2080	C-57
14b				94.7	20	2260 ^a	C-57
L-15a	12-22-58	Removed 4-7-59	2155	91.6	20	1620	C-58
15b				89.7	20	2055 ^a	C-58
L-18a	4-28-59	Removed 6-29-59	1324	84.9	30	c	C-42
18b				85.2	30		C-42
L-17a	4-7-59	Removed 8-10-59	2695	93.7	30	2410	C-58
17b				93.8	30	2600 ^a	C-58
L-11a	7-7-59	In operation		85	20	2140	C-47
11b				85	20	2575	C-47
L-16a	6-16-59	In operation		95	30	1950	C-57
16b				95	30	2050	C-57
L-18xa	7-7-59	In operation		85	30	2200	C-42
18xb				85	30	2450	C-42
L-21a	8-11-59	In operation			20	1460	C-58
21b					20	1690	C-58
L-20xa	8-18-59	Ruptured on startup,		75	15		C-28
20xb		removed 8-18-59		75	15		C-28
L-10	8-18-59	In operation		95	20	2800	C-44

^aEstimated from capsule wall and "a" capsule center temperature measurements.^bCalculated temperature 3000°F; rhenium-tungsten thermocouple failed during heatup.^cCalculated temperature 2760°F; rhenium-tungsten thermocouple failed during heatup.

Table 25. Fission Gas Release from LITR Capsules

Capsule Number	Central UO ₂ Temperature (°F)	Temperature Difference Across UO ₂ (°F)	Pellet Enrichment (% U ²³⁵)	Irradiation Flux (neutrons· cm ⁻² ·sec ⁻¹)	Burnup (Mwd/MT)	UO ₂ Density (% of theoretical)	Fission Gas Existing at Time of Reactor Shutdown (disintegrations/min)					Percentage of Existing Fission Gas Which Escaped from the UO ₂				
							Kr ^{85m}	Kr ⁸⁸	I ¹³¹	Xe ¹³³	Xe ¹³⁵	Kr ^{85m}	Kr ⁸⁸	I ¹³¹	Xe ¹³³	Xe ¹³⁵
× 10 ¹³																
UO ₂ -1-1*	1760	100	15	1	4,000	96	3.2 × 10 ¹²		5.8 × 10 ¹²	1.4 × 10 ¹³	5.6 × 10 ¹²	0.026		1.3 × 10 ⁻⁴	9.1 × 10 ⁻³	2.4 × 10 ⁻³
UO ₂ -1-2a*	1770	280	15	3.1	11,000	96		2.4 × 10 ¹³	1.9 × 10 ¹³	4.2 × 10 ¹³	7.8 × 10 ¹²	0.01		2.7 × 10 ⁻⁶	0.033	0.012
UO ₂ -1-2b*	2000		15	3.1	11,000	97		2.4 × 10 ¹³	1.9 × 10 ¹³	4.2 × 10 ¹³	7.8 × 10 ¹²	0.02		4.9 × 10 ⁻⁶	0.033	0.012
L-1a**	1600	300	10	2.8	8,000	95										
L-1b**	2100		10	2.8	8,000	95										
L-14a	2100	300	20	1.6	6,000	95	8.5 × 10 ¹²	2.1 × 10 ¹³	1.7 × 10 ¹³	3.8 × 10 ¹³	1.1 × 10 ¹³	0.029	0.011	1.3 × 10 ⁻⁵	0.014	0.006
L-14b	2200		20	1.6	6,000	95	8.5 × 10 ¹²	2.1 × 10 ¹³	1.7 × 10 ¹³	3.8 × 10 ¹³	1.1 × 10 ¹³	0.057	0.019	1.7 × 10 ⁻⁵	0.029	0.017
L-15a	1600	200	20	1.4	7,000	95	7.1 × 10 ¹²	1.8 × 10 ¹³	1.6 × 10 ¹³	3.2 × 10 ¹³	1.0 × 10 ¹³	0.019	0.004	5.5 × 10 ⁻⁵	0.010	0.004
L-15b**	1900		20	1.4	7,000	95										
L-2a**	2400	500	20	2.5	4,000	85										
L-2b	2500		20	2.5	4,000	85				5.0 × 10 ¹³					9.0	
L-4a	1600	200	10	1.5	13,000	95	6.9 × 10 ¹²	1.7 × 10 ¹³		3.1 × 10 ¹³	6.3 × 10 ¹²	0.011	0.021		0.028	8.5 × 10 ⁻³
L-4b	1900		10	1.5	13,000	95	7.0 × 10 ¹²	1.7 × 10 ¹³		3.1 × 10 ¹³	6.4 × 10 ¹²	0.012	0.020		0.04	7.5 × 10 ⁻³
L-6a	2200	300	10	2.5	13,000	75	5.4 × 10 ¹²			2.4 × 10 ¹³	4.9 × 10 ¹²	0.091			0.29	0.049
L-6b	2500		10	2.5	13,000	75	5.3 × 10 ¹²			2.4 × 10 ¹³	4.9 × 10 ¹²	0.035			0.13	0.026

*Data reported previously were miscalculated and have been corrected.

**Capsule L-1 was used only for the postirradiation heatup experiment; capsules L-15b and L-2a had lost their gas.

Table 26. Evolution of Solid Fission Products by Postirradiation Heat Treatment

	Fission Product Isotope					
	Nb ⁹⁵	Zr ⁹⁵	I ¹³¹	Cs ¹³⁷	Sr ⁸⁹	Ru ¹⁰³
Capsule L-1						
Total fission product isotope activity at time of reactor shutdown, disintegrations/min	2.8×10^{13}	4.4×10^{13}	3.0×10^{13}	4.3×10^{11}	2.2×10^{13}	2.4×10^{13}
Percentage of fission product isotope evolved by postirradiation heating to 2100°F	0.16	0.05	12.4	11.4	0.02	0.007
Capsule L-14						
Total fission product isotope activity at time of reactor shutdown, disintegrations/min	1.7×10^{13}	3.7×10^{13}	3.3×10^{13}	3.0×10^{11}	3.0×10^{13}	2.3×10^{13}
Percentage of fission product isotope evolved by postirradiation heating to 2500°F	0.005	0.007	7.4	5.5	0.01	0.001

Measurements of fission products from LITR experiments to date have involved the use of beta- and gamma-ray spectrometry or ion chamber measurements. The stable fission products have not been reported previously because their concentrations in samples of gas taken directly from the capsules were too small to be measured on the mass spectrometer when the concentration of radioactive products was low enough for safe handling. An apparatus has been constructed which will remove nonfission gas contaminants and concentrate the xenon and krypton by means of a Toepler pump (see Fig. 151). Gas samples have been saved from most of the LITR experiments and will be processed (as soon as most of the radioactive components have decayed) to obtain suitable mass spectrometer samples. One sample taken from L-14 during postirradiation heat treatment has already been analyzed. Relative quantities of the isotopes of xenon and krypton are given in Table 27 and compared with the values predicted by the graphs compiled by Blomeke and Todd.² Absolute values will not

be available until the Kr⁸⁵ is analyzed by gamma-ray spectrometry.

INSTANTANEOUS FISSION GAS RELEASE EXPERIMENT

R. M. Carroll C. D. Baumann

The ability of fuel materials to retain fission products is of great importance to reactor design. The following experiment was designed to study the continuing release of fission products from bare fuel materials at high temperatures and as a function of temperature, power, and volume-to-surface ratio of the fuel. Testing of the first fuel material, ThO₂-4% UO₂, is in progress. The next material to be examined will be UO₂.

The experiment is installed in position C-1 of the ORR, and the fuel is heated by fission and gamma heat. Evolved fission products are entrained in a helium sweep gas and carried outside the reactor for analysis. Power generated in the fuel is controlled by positioning the sample vertically in the reactor to obtain the desired flux. The temperature, for a given power, is attained by regulating the flow of cooling air past the capsule. The rate of flow of the sweep gas can be varied to determine the half lives of short-lived fission products. Fission products evolved from

²J. O. Blomeke and M. F. Todd, *Uranium-235 Fission-Product Production as a Function of Thermal Neutron Flux, Irradiation Time, and Decay Time*, ORNL-2127 (Aug. 19, 1957).

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Fig. 151. Fission-Gas Purification Train.

Table 27. Relative Abundance of Xenon and Krypton Isotopes Evolved from UO_2

Isotope and Mass	Relative Abundance (%)	
	Predicted*	Experimental (L-14)
Xenon		
131	10.3	11.54
132	17.4	18.59
134	31.2	32.05
136	41.1	37.82
Krypton		
82	0.001	0.35
83	11.8	14.49
84	27.8	27.92
85	7.1	6.89
86	53.3	50.35

*J. O. Blomeke and M. F. Todd, *Uranium-235 Fission-Product Production as a Function of Thermal Neutron Flux, Irradiation Time, and Decay Time*, ORNL-2127 (Aug. 19, 1957).

the sample are carried past a high-level G-M counter and an NaI-crystal scintillation counter. The output of the scintillation counter is fed to a single-channel pulse-height analyzer. A layout of the experiment is shown in Fig. 152. A flow diagram is shown in Fig. 153.

The activity of the fission products in the gas stream was unexpectedly high. This was not predicted by capsule tests, which had measured only longer-lived isotopes. The activity of the entrained fission products, at a constant fuel temperature and power, was measured as a function of the time required for the sweep gas to travel from the fuel sample to the counter (see Fig. 154). At decay times of the order of 0.5 min, the half life of the gas is about 0.5 min. At decay times between 2 and 5 min, the half life of the gas is around 2 min. Although these short-lived gases would reach production-decay equilibrium rapidly, the fuel was allowed to remain under the same conditions for 175 hr to see if the increasing contribution of longer-lived isotopes would be detected. No significant change was measured up to 5 min delay time, which is the minimum sweep velocity available.

Fig. 152. Instantaneous Fission Gas Release Experiment Layout in the ORR.

Fig. 153. Flow Diagram for Instantaneous Fission Gas Release Experiment.

A high-level G-M counter was used to obtain the data given in Fig. 154; this counter was periodically calibrated with standard Co^{60} sources. For this system, 1 mr/hr is equivalent to 1.86×10^4 photons (of Co^{60}) per second for each cubic centimeter of gas.

By allowing a trapped sample of gas to decay and observing the half lives and gamma energies, the following isotopes were identified: Kr^{85m} , Kr^{87} , Kr^{88} , Xe^{133} , Xe^{135} , Xe^{138} , Cs^{138} , Rb^{88} , I^{131} , and La^{140} . Other isotopes were present but could not be identified. Since none of the above products have half lives of less than 17 min, it is obvious (from Fig. 154) that they are not a dominating factor in the high activity of the evolved gas.

Because of the short half life of the gross fission product gas, it is apparent that the gas could not have spent much time in getting out of

the sample. The calculated activities of gross fission products, at 1 min decay time after fission, gave a half life of approximately 0.7 min, in approximate agreement with the measured value.³ These observations lead to the speculation that the greater part of the fission release is due to direct recoil. A diffusion process is temperature dependent, but a recoil release should not be affected by temperature. In order to determine the nature of the fission product release, the sample was maintained at constant power while the temperature was decreased by increasing the cooling air flow. The activity of the sweep gas, at a constant helium flow, was plotted as a function of temperature (Fig. 155). The non-temperature-dependent portion of the curve is due

³Gas-Cooled Reactor Project Semiann. Prog. Rep. Dec. 31, 1958, ORNL-2676, p 135-37.

Fig. 154. Gross Fission Product Activity from $\text{ThO}_2\text{-UO}_2$.

both to recoils and to fission products (primarily iodine) that plate on the walls of the system and then decay to a product that is released.

The activity of fission gas released from a fuel by a diffusion process should be proportional to an exponential function of the reciprocal of the temperature. The constant non-temperature-dependent contribution is subtracted from the total activity and the difference plotted vs the reciprocal of the temperature in Fig. 156. The conclusion is that the diffusion process of fission product release dominates at temperatures above 1300°F .

The short-lived products that are released by diffusion, which dominate the observed activity, may have diffused only a short distance. The observed activity represents only about 30% of the total expected 40 sec after fission for all fission products from a depth of 9.4×10^{-4} cm (the recoil distance in the fuel).

The spectrum of the gases evolved from the fuel is too complicated for direct quantitative analysis

Fig. 155. Activity of Fission Products as a Function of Fuel Temperature.

by gamma-ray spectrometry. A system of traps has been installed to remove all fission gases except krypton from the helium sweep. This trap system is controlled remotely and can be used to measure gross activity, xenon and krypton, or krypton only.

Krypton measurements made on trapped gas from the $\text{ThO}_2\text{-UO}_2$ sample show escape of about 0.06% of the Kr^{88} formed, in the $1700\text{--}1900^\circ\text{F}$ range. Very small temperature dependence was observed. Xenon-133 escapes at a greater rate, by a factor of 5. About 0.3% of the Xe^{133} formed escaped at 1680°F . The Xe^{133} escape appeared highly temperature dependent.

The next experiment will be performed with plates of UO_2 , 1 in. long, 0.65 in. wide, and 0.032 in. thick (see Fig. 157). Two plates are placed together so that two thermocouples are sandwiched between them. Thermocouples are also pressed against the outer surfaces of the sample. The temperature difference between the outer and

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Fig. 156. Fission Product Activity vs Reciprocal Temperature.

inner surfaces may be useful for a rough measurement of thermal conductivity as a function of irradiation.

CLOSED-CYCLE GAS-COOLED EXPERIMENT

P. E. Reagan H. P. Moser⁴

The experiment, described previously,⁵ was installed in the ORR, and a series of performance tests were conducted. By using $\text{Cr-Al}_2\text{O}_3\text{-UO}_2$ cermet plates for a heat source in the B-9 lattice position, flow and compressor characteristics were established. Compressor rod seal leakage proved the most bothersome problem, although there was some temperature-pressure feedback which caused control oscillations. Two special compressors

⁴On loan from Reactor Ltd., Wuerenlingen, Switzerland.

⁵Gas-Cooled Reactor Project Semiann. Prog. Rep. Dec. 31, 1958, ORNL-2676, p 120.

have arrived which will eliminate the excessive seal leakage problem. The first samples to be tested are UO_2 pellets canned in graphite and coated with SiC-Si . The experiment is ready to go into operation at the present writing.

HOT CELL MODIFICATIONS

H. E. Robertson M. F. Osborne
T. W. Fulton

The structural changes have been completed on a modified hot cell to examine irradiated samples containing plutonium. The in-cell equipment is ready for installation. The plan of the altered cell is shown in Fig. 158. Two viewing windows and three master-slave manipulators allow the entire floor area of the cell to be utilized. The rear rotary door provides access for radioactive samples into the cell. Samples will be removed through a wash station, not shown, using the same door. The cell is provided with rear access plugs, bridge crane, and a rear gamma-shield door for access into the decontamination room. In this room, equipment may be repaired and decontaminated by use of glove ports and a viewing window. The cell and decontamination room have a filtered ventilation system separate from the rest of the cells in that area. Personnel will be restricted to the rear room. Equipment will be provided to measure the pressure and volumes of fission gas released from samples, the profile of the sample containers, and the density of the test materials. A remote slitting and machining apparatus will be used for opening the fuel containers, and metallographic equipment will prepare polished samples for photomicrographs.

Equipment has also been developed for use in the hot cell in the ORR building. Here, experiments withdrawn from the ORR will be disassembled and the fuel capsules prepared for removal to the Solid State Division hot cell. This equipment has already been checked out on flux depression experiments.

GRAPHITE AND GRAPHITE COATINGS

R. M. Carroll

In some of the advanced gas-cooled reactor concepts the fuel material is canned in graphite. New high-density and low-permeability graphites are being developed for this application, and, for reactors which are operated at high temperatures

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Fig. 157. Fuel Capsule Assembly for Instantaneous Fission Gas Release Experiment.

L E G E N D

	EXISTING REGULAR CONCRETE.		EXISTING STEEL.
	EXISTING HIGH-DENSITY CONCRETE.		NEW STEEL (REGULAR).
	NEW HIGH-DENSITY CONCRETE.		NEW STEEL (STAINLESS).
	EXISTING HIGH-DENSITY SOLID CONCRETE BLOCK.		NEW LEAD.
	NEW HIGH-DENSITY SOLID CONCRETE BLOCK.		
	NEW REGULAR SOLID CONCRETE BLOCK.		

SCALE IN FEET

C-32495

NOT CLASSIFIED

PLAN
ALTERATION TO CELL 6 — BUILDING 3025
OAK RIDGE NATIONAL LABORATORY

DRAWING B

Fig. 158. Remodeled Hot Cell for Fuel Materials Studies.

in an oxidizing atmosphere, it is necessary to coat the graphite with an oxidation-resistant material. Radiation effects studies on the new low-permeability graphites are just getting under way. Some work has already been done on an SiC-Si-coated graphite which was developed by J. R. Johnson of the Minnesota Mining and Manufacturing Company.

Out-of-pile tests⁶ have shown small samples of this material to be unaffected for periods up to 1000 hr in air at 2000°F. Near-sonic air blasts at 1830°F did not produce erosion damage, and rapid thermal cycling from 1830°F to room temperature did not crack or damage the specimen.

The coating on the graphite was demonstrated to be gastight, according to weight loss measurements vs time at elevated temperatures. To determine the effect of an internal pressure, such as might be produced by buildup of fission gas upon the cladding, a special sample was prepared. A 6-in.-long graphite tube, $\frac{1}{2}$ in. OD $\times$ $\frac{1}{4}$ in. ID, closed at one end, was coated on the outside only and threaded at the open end. The threaded end of the tube was copper plated and then screwed

and silver soldered onto an Inconel tube. A platinum-wound heater was placed over the lower 3 in. of the tube. The graphite tube was pressurized to 100 psig with helium and the temperature brought to 2000°F. The system was periodically checked for leaks by closing off the helium supply and observing the pressure. After 1050 hr at 2000°F, the tube was examined, and no evidence of damage was found. No detectable leakage of helium had occurred.

Two coated graphite cylinders irradiated to 6×10^{19} neutrons/cm² were found to be practically unchanged in density. Oxidation tests indicated that the coating was intact. These cylinders were replaced in the reactor and irradiated to 5×10^{20} neutrons/cm² at reactor water temperatures. At discharge the cylinders had a decrease in density of 1%. One of the cylinders appeared unchanged, but the other had a blistered appearance (Fig. 159). The blistered sample had a metallic appearance before irradiation (sample A, Fig. 160). When the blistered sample was immersed in CCl₄, bubbles were observed and the weight of the sample increased with time of immersion, indicating cladding failure. The other sample was oxidation tested for 207 hr at 2000°F, without

⁶*Ibid.*, p 132.

Fig. 159. One of Two SiC-Si-Coated Graphite Cylinders That Were Irradiated to an *nvt* of 5×10^{20} . Sample A blistered; the other sample was unchanged.

Fig. 160. SiC-Si Coated Graphite Rods Before Irradiation.

weight change. This sample returned to its pre-irradiation density after the high-temperature annealing.

Two more samples, which had been irradiated to 6.3×10^{20} neutrons/cm² at reactor water temperature, have now also been taken out of the reactor. The densities of these specimens had decreased by 2%. Both specimens appeared sound and did not exhibit leaks when placed in hot silicone oil. These specimens have been tested for oxidation resistance at 2000°F in air for 186 hr, and no weight change was observed (± 0.0007 g). These samples also returned to their original density during the 2000°F oxidation test.

THERMOCOUPLE IRRADIATION STUDIES

C. D. Baumann

The change in response of thermocouples due to neutron exposure is of obvious interest in high-temperature fuels studies. Both base-metal (Chromel-Alumel) and noble-metal (platinum vs platinum-10% rhodium) thermocouples have been irradiated in the LITR, ORR, and MTR up to exposures of 4×10^{20} nvt thermal, and the change in thermal response measured after irradiation. The error in emf output of the platinum vs platinum-10% rhodium couples depends upon the location of the thermal gradient with respect to

rhodium transformation, as well as upon the time-integrated exposure. The change in emf output of irradiated Chromel-Alumel thermocouples did not exceed the $\frac{3}{4}\%$ commercial tolerance for unirradiated wires.

Either short thermocouples, 15 to 18 in. long, or clusters of three wires of the same material welded together at one end were inserted in weld-sealed aluminum capsules. The capsules were irradiated in the C-47 hollow beryllium piece adjacent to the active lattice of the LITR or in a similar B-9 piece in the ORR for the desired number of reactor cycles.

A cluster of three irradiated Chromel or Alumel wires was welded to an unirradiated wire from the original spool by means of a remotely operated thermocouple welder (Fig. 161). The cluster of four wires was inserted in a furnace (Fig. 162) and the difference emf between the unirradiated and one of the irradiated wires was obtained as a function of temperature. At least three complete sets of error-vs-temperature plots were obtained for each irradiated wire from ambient to 1000°C and back to ambient. Generally, for a given time-integrated exposure, the error emf for Alumel wire was greater in magnitude, and in percentage deviation, than for Chromel wire. The errors at all exposures up to 4×10^{20} nvt tend to be

compensating (rather than additive) in the complete couple and less than or approximately equal to the $\frac{3}{4}\%$ tolerance for unirradiated wires.

Fig. 161. Remote Thermocouple Welder.

Fig. 162. Remote Calibration of Thermocouples.

The method of attaching an unirradiated wire to a cluster of irradiated Chromel or Alumel wires was not satisfactory for platinum or platinum-rhodium wires. The normal method of fabricating couples (arc welding in a protective atmosphere — used by the Standards Laboratory of the Instrument Department) was used to attach an unirradiated couple to the irradiated cluster or couple. The wires were then insulated and calibrated by the ORNL Instrument Department Standards Laboratory by the routine methods for calibrating standard platinum-platinum-rhodium thermocouples. The results for the normal calibration, using a 24-in. tube furnace (12 in. of thermocouple immersion), are shown in Figs. 163 and 164. A summary of error emf's at 10 mv output (1900° F), as measured in a 7-in. tube furnace, 3½-in. immersion, is shown in Fig. 165.

In comparing Figs. 165 and 164, it becomes apparent that the location of the temperature

Fig. 163. Effect of Irradiation on Platinum vs Platinum-10% Rhodium Thermocouple. Bishop wire, measured in 24-in. tube furnace (12-in. immersion).

Fig. 164. Effect of Irradiation on Platinum vs Platinum-10% Rhodium Thermocouple. Sigmund Cohn wire, measured in 24-in. tube furnace (12-in. immersion).

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gradient, with respect to the neutron flux gradient, has a great effect upon the error emf. The furnace-temperature gradient in Fig. 165 is much closer to the junction of the couples than is the gradient in Fig. 164, hence the temperature gradient in the short furnace occurs in a region of higher rhodium transmutation than it does in the normal furnace used for obtaining the data listed in Fig. 164. Thus the error is greatest when the temperature gradient occurs at the point of the highest integrated-flux exposure. This is more clearly shown by comparing the Cohn with the L & N couples of Fig. 166. The L & N couples received a uniform neutron dosage throughout their length, whereas the Cohn couple dosage varied over its length, with the maximum near the junction of the couples.

Additional Sigmund Cohn couples have been irradiated in the ORR to 4×10^{20} nvt, but their activity after eight months of decay is still too high to permit calibration by standard methods.

Fig. 166. Error EMF of Platinum vs Platinum-10% Rhodium Thermocouples vs Temperature. Measured in a 7-in. tube furnace ($3\frac{1}{2}$ -in. immersion).

Fig. 165. Error Observed from Platinum vs Platinum-10% Rhodium Thermocouple in 7-in. Tube Furnace ($3\frac{1}{2}$ -in. Immersion) at 1900°F as a Function of Neutron Exposure.

BRITTLE FRACTURE OF METALS

J. C. Wilson

This is a new project less than a month old, and the work to date has been confined to experiment planning and completing tests of a number of pertinent specimens irradiated earlier on HRP and GCR projects. New or improved apparatus for hot-cell testing, for measurement of delay time for plastic deformation, and for internal friction measurements on tensile specimens are being designed or built.

Embrittlement (or significant loss of useful ductility) of metals by irradiation has been observed in a number of metals and alloys as follows:¹

1. In iron, steels, and other body-centered cubic metals the transition temperature (from ductile, shear fracture to brittle, cleavage fracture) may be greatly increased by irradiation.
2. In steel, high neutron doses at high irradiation temperatures (on the order of 300°C and higher) have produced intergranular fractures in pearlitic steels at low strains in room-temperature tensile tests.
3. In irradiated nickel, embrittlement (believed to be caused by intergranular fracture) has been observed.
4. In high-temperature creep of Inconel, grain boundary embrittlement of an unknown mechanism has been observed to shorten the rupture life.
5. In many face-centered cubic, body-centered cubic, and hexagonal metals irradiation causes a marked decrease (sometimes almost to zero) of the uniform elongation: that is, the elongation before necking begins. Although the fractures may not be truly brittle, the irradiated metals are effectively brittle for engineering purposes, because fracture may take place with decreasing load after yielding: the general deformation and high level of plastic energy absorption of a truly ductile metal are lacking.
6. It seems possible for the irradiation-induced strain-rate (or temperature) dependence of the

yield stress in face-centered cubic metals to allow easier crack initiation by raising the yield stress relative to the fracture stress, particularly at high deformation rates.

It appears that there are a number of mechanisms by which irradiation may cause brittle, or effectively brittle, fractures in metals used in reactors. Probably the most important effect at present is the irradiation embrittlement of steels and possibly other body-centered cubic metals.

Although b.c.c. metals other than iron have certain advantages for study of radiation embrittlement, iron will be used initially because of its relevance to radiation effects in pressure-vessel steels and because it is by no means certain that some of the other b.c.c. metals that appear less complicated than iron are really so. It may be that the complexities have not yet been discovered.

Iron (and its alloys) appear particularly interesting because it has been shown that radiation effects (measured by the transition temperature increase) in high-purity iron and high-purity iron alloys are much less than in steels of equivalent carbon content. The large increases in transition temperature of commercial steels must, in large part, be due directly or indirectly to impurity effects. A thorough understanding of the purer iron and iron alloys must be obtained in order to study the effects in steels. Comprehensive data on the mechanical properties of iron in the literature are confusing and outdated.

The initial work will be confined to iron (vacuum-melted, zone-refined, and decarburized steels) with variable carbon and nitrogen contents. The mechanical properties will be determined as a function of temperature and strain rate, and the delay time for initiation of plastic deformation will be measured. Internal friction or magnetic methods will be used to follow the progress of carbon and nitrogen precipitation. Working and heat-treating

¹J. C. Wilson, *Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy*, 2nd, Geneva, 1958 5, 431 (1958).

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cycles will be developed to give variations in grain size, substructure, and dispersion of carbon or nitrogen precipitates.

The data obtained will define the mechanical properties of iron over a wide range of conditions to serve as a base line for other studies. Particular attention will be given to achieving structures that are stable for periods of weeks or months at temperatures up to 300°C in order

to be able to study the effects of irradiation temperatures separately from thermal effects.

When the properties of iron and its alloys can be reproduced and predicted over a wide range of conditions it will then be possible for the first time to study the effects of irradiation, irradiation temperatures, and state of the material with less complications than are known to have obfuscated interpretation of earlier data on steels.

RADIATION METALLURGY

J. C. Wilson

O. Sisman

The radiation metallurgy program is reported primarily in two parts. The brittle fracture work, as in the past, is mainly concerned with evaluating the effect of fast-neutron irradiation on steels and welds used in pressure-vessel construction. The effect of fast-neutron irradiation on the stress-rupture life is being determined for Inconel and stainless steel, and a number of other metals are being added to this program. During the past year all of the irradiation programs have been transferred from the MTR to the ORR, and improved instrumentation has been developed for these experiments along with the development of the new facilities.

Both the stress-rupture and the brittle fracture irradiations in the ORR are performed in the pool-side facility. Use of the pool-side irradiation facility has indicated that the experiments previously conducted in beam holes of the MTR and LITR can be more expeditiously conducted in this ORR facility. By proper positioning of the experiment in the pool-side facility, fast-neutron fluxes can be obtained in the experiment that are equivalent to those obtained in experiments in either the MTR or the LITR beam holes. As a result, experiments are mounted "piggy-back" to achieve simultaneous exposure at various flux levels and to increase specimen capacity.

Temperature control of the stress-rupture experiments has proved quite troublesome because of changes in reactor power. Satisfactory instrumentation has now been worked out which will automatically control the temperature of the specimens within the limits desired, even with large changes in reactor power. This instrumentation is now being installed on all stress-rupture experiments.

GCR BRITTLE FRACTURE OF METALS

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Two irradiation experiments have been conducted in the ORR and several more in the LITR.

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A large backlog of specimens remain to be tested from these irradiations, but most of the earlier MTR and LITR irradiations have now been processed in the hot cell. The objectives sought in this irradiation program are to determine the variations of sensitivity to irradiation of several steels, the effect of elevated temperature, and the effects of postirradiation annealing.

Brittle fracture studies have shifted from an emphasis on subsize Izod tests to standard-size Charpy V-notch tests. The reasons for this change are: (1) Subsize specimens were used originally because of the limited irradiation space available. This consideration has now become a minor factor. (2) A large body of data exists correlating Charpy-V tests with service behavior. Such correlation data do not exist for subsize impact tests. (3) The Charpy V-notch test is a standard in many laboratories and well accepted, while there is no uniformity among the numerous subsize tests.

The Charpy V-notch impact properties of several steels irradiated at temperatures from 175 to 330°F, to fast-neutron doses up to 1×10^{20} nvt (>1 Mev) were determined as a function of fast-neutron dose. The results, given in Figs. 167-174, show the now familiar rise in impact transition temperature and decrease of ductile energy absorption with increasing irradiation dose. There is a very striking similarity in the changes observed for the commercial steels (Figs. 167-172). The change of impact transition temperature (10 ft-lb level) is plotted in Fig. 175 as a function of the neutron dose to which the specimens were exposed. Included on this plot are data for all Charpy-V irradiation experiments, conducted on a variety of steels (listed in Table 28) at irradiation temperatures up through 330°F. The data for all but two (items 60 and 111) of the steels fall within a relatively narrow band. Above about 10^{18} nvt the changes of impact transition temperature are a linear function of the logarithm of the exposure for this temperature range. A similar plot is obtained for the drop in energy absorption above the transition temperature as a function of exposure.

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Fig. 167. Charpy-V Impact Strength of Irradiated ASTM A-212 Grade B Carbon-Silicon Steel. Hot-rolled condition. Item 43.

Fig. 168. Charpy-V Impact Strength of Irradiated ASTM A-212 Grade B Carbon-Silicon Steel. Normalized from 1700°F. Item 43.

Fig. 169. Charpy-V Impact Strength of Irradiated ASTM A-285 Grade A Carbon Steel. Hot-rolled condition. Item 44.

Fig. 170. Charpy-V Impact Strength of Irradiated ASTM A-285 Grade A Carbon Steel. Normalized from 1700°F. Item 44.

Fig. 171. Charpy-V Impact Strength of Irradiated ASTM A-301 Grade B Chromium-Molybdenum Steel. Item 45.

Fig. 173. Charpy-V Impact Strength of Irradiated Iron-Carbon Alloy. Air-cooled from 1650°F. Item 111.

Fig. 172. Charpy-V Impact Strength of Irradiated $2\frac{1}{4}\%$ Chromium Steel, ASTM A-200-55T Grade T-22. Item 49.

The shift in transition temperature as measured by subsize Izod impact tests on many of the same steels differs somewhat from the Charpy data of Fig. 175. Subsize Izod data indicated slightly greater changes at about 2×10^{18} nvt and, about 100°F, less change at 1×10^{20} nvt. Thus the slope of the curve for the subsize Izod data was less than for full-size Charpy-V data. Because of the large difference in geometry between the two specimens each may be affected to a different degree by certain phenomena, such as crack initiation at the root of the notch, brittle crack propagation in the interior of the specimen, and shear failure at the sides of the specimen ("shear lip").

The steel designated "item 60" is from an early heat of a high-strength, quenched and tempered structural steel known as Carriloy T-1. The change in transition temperature of this steel as a result of irradiation was greater than for the other steels tested, but its final transition temperature was approximately the same as for the other

Fig. 174. Charpy-V Impact Strength of Irradiated Iron-Carbon Alloy. Air-cooled from 2000°F. Item 111.

steels tested because of a much lower initial transition temperature. Early heats of this steel are believed to vary considerably in properties, and since item 60 is from an early heat, these data may not be typical of the present-day product. Irradiation results are not yet available on a more recent heat of this steel.

The steel designated "item 111" is a vacuum-melted high-purity iron-carbon alloy (Table 28). This steel showed much less change of impact transition temperature than the commercial steels exposed to the same integrated neutron flux (see Fig. 175, item 111). The results for this material, Figs. 173 and 174, are very similar to the subsized Izod impact results for the supercritical annealed high-purity iron reported previously³ in that there is only a small change in transition temperature and that no observable drop in energy absorption

³J. C. Wilson et al., *Solid State Ann. Prog. Rep.* Aug. 31, 1958, ORNL-2614, p 98.

Fig. 175. Effect of Fast-Neutron Irradiation on Charpy-V Impact Transition Temperatures of Several Steels.

occurs above the transition temperature. It appears, therefore, that metal purity has considerable effect on the response to irradiation and that there is hope of improving properties of irradiated steels by control of alloy composition.

The Effect of Elevated Temperature

Studies of the effects of elevated irradiation temperatures on the brittle fracture properties of steel have continued. Results obtained this year have substantiated the previous conclusion³ that irradiation at 575°F leads to less change than irradiation at lower temperatures but that these effects vary even in steels of similar types. Factors controlling this variation of response to elevated irradiation temperature have not been determined.

Charpy V-notch impact specimens from the lid forging, carbon steel plate, and welds for the Halden Reactor (Norway) were made available for irradiation tests. The lid forging (Table 29, item 141) was 132 in. in diameter and 28 in. thick and was forged at approximately 1200°F to ASTM standard A-105-55T. Specimens were taken from

Table 28. Impact Test Steels

Item No.	Description	Chemical Composition (%)					
		C	Mn	P	S	Si	Others
18	ASTM A-212 grade B carbon-silicon steel; $\frac{1}{2}$ -in. plate; normalized	0.24	0.81	0.020	0.040	0.248	
43	ASTM A-212 grade B carbon-silicon steel; $\frac{5}{8}$ -in. plate	0.20	0.82	0.018	0.030	0.22	
44	ASTM A-285 grade A carbon steel; $\frac{3}{4}$ -in. plate	0.11	0.32	0.018	0.020		
45	ASTM A-301 grade B chromium-molybdenum steel; $\frac{3}{4}$ -in. plate	0.11	0.36	0.020	0.026	0.22	0.98 Cr; 0.47 Mo
49	ASTM A-200 grade T-22 Croloy $2\frac{1}{4}$ -in. alloy steel pipe. $\frac{1}{2}$ in. wall by 6 in. OD	0.10	0.45	0.018	0.019	0.031	2.18 Cr; 1.00 Mo
60	High-strength quenched and tempered steel (Carriloy T-1)						Not available
92	ASTM A-212 grade B carbon-silicon steel; $\frac{3}{4}$ -in. plate						Not available
111	High-purity iron-carbon alloy; $\frac{3}{4}$ by $3\frac{3}{4}$ in. bar	0.180	0.002	<0.003	0.003	0.03	0.0039 O; 0.0003 H; 0.0001 N; other metals ≤ 0.01
115	ASTM A-212 grade B carbon-silicon steel; $6\frac{1}{4}$ -in. plate	0.27	0.82	0.016	0.028	0.19	
127	ASTM A-302B manganese-molybdenum steel; $8\frac{1}{2}$ -in. plate	0.19	1.36	0.020	0.025	0.26	0.48 Mo
133	Swedish 2112 carbon-silicon steel; $3\frac{3}{4}$ -in. plate	0.16	1.29	0.012	0.031	0.32	0.08 Cr; 0.08 Ni; 0.14 Cu

Table 29. Halden Reactor Steels

Item No.	Description	Chemical Composition (%)						
		C	Mn	P	S	Si	Cr	Cu
141	ASTM A-105-55T steel forging	0.23	0.56	0.016	0.021	0.21		
142	ASTM A-212 grade B carbon-silicon steel plate	0.19	1.25	0.013	0.040	0.26	0.03	0.19
143	Weld metal; low-hydrogen basic type							Not available

the surface of this forging. The carbon steel plate (Table 29, item 142) is the 60-mm-thick mild steel component of the compound plate used for the reactor pressure vessel and was manufactured to ASTM standard A-212 grade B. It was normalized, welded, and stress-relieved (about 1200°F). The weld metal was tested separately. The weld metal was deposited with electrodes⁴ of the low-hydrogen basic type similar to American E-7016 electrodes. Charpy V-notch specimens of these steels were irradiated at 390°F in two positions in the HB-3 facility of the LITR. The values for thermal flux in Table 30 are from cobalt monitors in this experiment; the values for fast-neutron flux (>1 Mev), Table 30, are based on values previously obtained in this facility. The results of these experiments are given in Figs. 176-178. These results are not plotted in Fig. 175 because of the elevated irradiation temperature but would fall slightly below the scatter band of Fig. 175. Data are not available for these steels irradiated at lower temperatures, but, if it is assumed that they would behave like the commercial steels for which data are plotted in Fig. 175, it appears that irradiation at 390°F results in less change than irradiation at less than 200°F. Results obtained in England⁵ from notch-bend tests of several steels indicated a greater change in transition temperature for irradiation at 270°F than at 100°F. Similar behavior has been observed here³ for irradiations of some steels at 440°F. Irradiation

effects in the temperature range from about 200 to 500°F, on the basis of the few data available, are an undetermined function of the material, irradiation dose, and irradiation temperature and may be either larger or smaller than the effects observed at irradiation temperatures less than 200°F, where the largest body of data exists.

Fig. 176. Charpy-V Impact Strength of Irradiated Halden Reactor Pressure-Shell Plate (ASTM A-212 Grade B). Item 142.

Table 30. Irradiation Conditions for Halden Reactor Steels

Reactor at power: 1413 hr
Irradiation temperature: 390°F

Specimen Position	Neutron Flux (nv)		Integrated Neutron Dose (nvt)	
	Thermal*	Fast**	Thermal	Fast
High flux	4.6×10^{12}	1.8×10^{12}	2.3×10^{19}	9×10^{18}
Low flux	2.8×10^{12}	9.7×10^{11}	1.4×10^{19}	5×10^{18}

*Bare cobalt monitors.

**> 1 Mev.

Fig. 177. Charpy-V Impact Strength of Irradiated Halden Reactor Lid Forging (ASTM A-105-55T). Item 141.

Postirradiation Annealing

Preliminary data from step-annealing of hardness specimens irradiated to 1×10^{18} nvt (> 1 Mev) at 140°F and to 5×10^{18} nvt at 140 and 575°F are given in Fig. 179 with similar data for unirradiated specimens of the same steel with 5% cold work. It may be noted that the annealing behavior of the specimens irradiated at 140°F is different than that for the cold-worked steel but that there is considerable similarity between the annealing behaviors of the cold-worked specimens and specimens irradiated at 575°F. Annealing of the specimens irradiated to 5×10^{18} nvt at 140°F was more rapid than for those irradiated to the same dose at 575°F, and, in fact, they became

Fig. 178. Charpy-V Impact Strength of Irradiated Halden Reactor Weld Metal (Low-Hydrogen Basic Type). Item 143.

Fig. 179. Postirradiation Annealing of Irradiated ASTM A-212 Grade B Carbon-Silicon Steel.

softer than those irradiated at the higher temperature. Some time- and temperature-dependent change had undoubtedly occurred during the 575°F irradiation such that the imperfections introduced by irradiation had changed character or distribution, resulting in a change of annealing kinetics. This study is being pursued further with isothermal annealing tests and annealing tests on Charpy-V and tensile specimens.

Comparison of Neutron Fluxes

It has been difficult to compare ORNL, Harwell, and Chalk River data on radiation effects in steels because the flux units differ. By comparing the yield strength increase as a function of integrated flux for Harwell, Chalk River, and ORNL it is possible to convert all data to a common base. ORNL data are reported for neutrons of energy greater than 1 Mev; sulfur monitors (effective threshold 2.9 Mev) are actually used and the values for 1 Mev deduced from spectral measurements made by Trice. If the Harwell fluxes (thermal neutrons) are divided by 10 and the Chalk River fluxes (above 500 ev neutrons) divided by 8, the damage in steels will be the same as a numerically equivalent ORNL (> 1 Mev) flux. Note that this is a comparison of damage in steels and is not intended to imply any comparisons of reactor flux. The relationship seems valid for (1) irradiations at less than 200°F, (2) Chalk River transformer rod irradiations, and (3) Harwell irradiations in BEPO. Chalk River or Harwell data for irradiations performed in other reactors have not been correlated to these conversion factors.

CREEP AND STRESS RUPTURE

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Details of the construction and operation of the tube burst tests were presented in the last Solid State Division progress report,⁶ along with a discussion of the method of neutron flux monitoring for these experiments, and some discussion of the meaning of the data. The series of tests to determine the effect of neutron bombardment on the rupture life of Inconel (started in the MTR) is continuing in the pool-side facility of the ORR. The specimens here are positioned horizontally in two parallel vertical columns with the specimen axes normal to the face of the reactor core. This arrangement permits assembly of ten specimens in a 14-in. vertical space, equally divided above and below the plane of maximum flux. Figure 180 shows an ORR tube burst experiment prior to insertion in the exposure can.

⁶J. C. Wilson *et al.*, *Solid State Ann. Prog. Rep.* Aug. 31, 1958, ORNL-2614, p 98.

Fig. 180. Assembled Tube Burst Experiment for the ORR. At the extreme left is the top plate of the exposure can. The capillary pressure tubes from the specimens can be seen emerging from the furnaces. The specimen ends located at the bottom of the photograph face the pool-side face of the reactor core when installed in the irradiation facility.

The ORR tube burst tests have been conducted at 1500°F in air. The data are presented in Table 31. Figure 181 is a graph of all the rupture data on Inconel tested in air at the MTR, at the ORR, and on the bench. The unirradiated test data are within the scatter band of the data reported by the Metallurgy Division. The graph shows a reduction in rupture life by a factor of 3 to 5 for the irradiated specimens. The reduction in strength for rupture is well over 1000 psi over the entire curve. Postirradiation examination of the ORR experiments is under way.

Postirradiation examination of the second MTR experiment⁶ has been completed. The total strain data exhibit very broad scatter. This is probably due to the effect of repressurizing the ruptured specimens, as previously reported.⁶ Inspection of the as-polished metallographic specimens revealed normal intergranular, high-temperature fracture for both the in-pile (Figs. 182 and 183) and out-of-pile tests (Figs. 184 and 185), except that the irradiated specimens appeared to have less ductility and the fractures were more localized.

The reduced ductility was also apparent in one irradiated specimen which fractured in a brittle manner during a cutting operation with an abrasive

Fig. 181. Stress vs Rupture Life of Inconel in Air at 1500°F.

Table 31. Effect of Neutron Bombardment on the Rupture Life of Inconel at 1500°F in Air: ORR Experiments

Specimen No.	Stress (psi)	Irradiation Dose at Rupture (Mwhr)*	Rupture Life (hr)
2-2	3000	10,000	470
2-5	5000	2,200	100
2-6	5000	2,000	91.5
4-1	2000	19,796	Not ruptured
4-2	2000	19,796	Not ruptured
4-3	2500	19,796	Not ruptured
4-4	2500	19,796	Not ruptured
4-5**	5000	4,285	109
4-6**	5000	13,230	110.5
4-7	6250	1,219	56
4-8	6250	975	43.5
4-9	3000	13,120	787
4-10	3000	12,884	774

*Integrated neutron flux may be estimated by multiplying the number of megawatt-hours by 4×10^{15} (thermal neutrons/Mwhr) or 1.3×10^{15} (fast neutrons/Mwhr). Cobalt and sulfur monitors will be counted shortly.

**These specimens were irradiated at temperature prior to application of stress.

Fig. 182. Transverse Section in the Fracture Region of an Inconel Tube-Burst Specimen Tested at 1500°F in Air at the MTR. The stress was 5000 psi and the rupture time was 94 hr. 100X. Reduced 50%.

Fig. 184. Transverse Section in the Fracture Region of an Inconel Tube-Burst Specimen Tested at 1500°F in Air Out-of-Pile. The stress was 4000 psi and the rupture life was 800 hr. 100X. Reduced 38%.

Fig. 183. Transverse Section in the Fracture Region of an Inconel Tube-Burst Specimen Tested at 1500°F in Air at the MTR. The stress was 5000 psi and the rupture time was 94 hr. Notice the scalloped edges of many of the grains along the major separations and the series of voids in the grain boundary prior to separation. 250X. Reduced 17%.

cutting saw. The irradiated specimens appeared also to contain bubble-shaped voids at grain boundaries both normal and parallel to the major stress direction and a fairly regular scalloped edge on the metal along the fracture. The scalloped edge appears to have been formed by the joining of adjacent voids to create a fracture path.

The appearance of these voids led to the suggestion that a gas is being produced in the metal and making its appearance at the grain boundary. It was further suggested that this gas is helium, produced by thermal-neutron capture in B^{10} . Spectrographic examination indicates that boron is present in the Inconel being tested in the range of 10 to 50 ppm by weight. The helium, collected into small gas pockets, would either weaken the grain boundary or act as stress raisers. In addition, the lithium by-product of the nuclear reaction might in some way (as the element or its oxide) reduce the ability for grain boundary deformation and thus cause separation at the grain boundary. Supporting evidence for this idea of gas voids is the observation of voids in boron stainless steel control rods (containing 1% boron)⁷ and in the braze material used until recently in the tests reported here. Figures 186 and 187 show the irradiated and unirradiated braze material. Many small voids are clearly indicated in and around the intermetallic boride areas.

Several investigations are under way in an effort to verify the theory that boron is responsible for the decrease in creep rupture life of Inconel. It is planned to test additional heats of Inconel with similar boron concentration but varying B^{10} concentration, and also to test materials with

⁷W. O. Schaffnit, *Radiation Damage Studies of Boron Stainless Steel*, IDO-16502 (Jan. 28, 1959).

Fig. 185. Transverse Section in the Fracture Region of an Inconel Tube-Burst Specimen Tested at 1500°F in Air Out-of-Pile. The stress was 4000 psi and the rupture life was 800 hr. This control specimen exhibited more ductility at the grain boundaries than the specimen shown in Fig. 183. 250X.

different boron content. It may be necessary to know whether or not the boron is concentrated at grain boundaries, and methods of determining this are being investigated. In the interim, two Inconel specimens from the same heat of material as previously tested have been given 100- and 550-hr irradiations, respectively, before subjecting them to stress (5000 psi at 1500°F). In the event that the specimen with the higher B^{10} burnup (longest unstressed irradiation) would have accumulated more gas or other impurities at the grain boundaries, it was thought that this specimen might show a shorter creep-rupture life. The calculated B^{10} burnups prior to stressing were 7 and 30%. No appreciable difference in rupture life was noted, but perhaps the difference in total atoms reacted was too small. Other specimens with greater amounts of B^{10} burnup will be tried. Other boron-containing alloys (type 304 stainless steel, type 304 ELC stainless steel, and INOR-8)

are being studied to determine if decreased rupture life and decreased ductility are observed in these alloys also.

Creep and stress-rupture studies have been initiated on beryllium. This is a potential fuel element canning material for several future gas-cooled power reactors. The expected fast-neutron dose for the life of the fuel element is 10^{21} neutrons/cm² or greater. Large changes may be expected in the properties of beryllium because of two reactions: an $(n,2n)$ reaction resulting in two atoms of helium, and an (n,α) reaction resulting in two atoms of helium and one of tritium. Approximately 2 cc of gas is produced per cc of beryllium at 10^{21} nvt fast.^{8,9}

⁸C. E. Ells, *The Swelling of Beryllium from Neutron-Induced Gases*, AECL-719 (November 1958).

⁹D. W. White, Jr., and J. E. Burke, *The Metal Beryllium*, American Society for Metals, Cleveland, 1955.

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Tube burst tests are planned for a core position in the ORR, and earlier experiments are planned for irradiation of beryllium both hot (500 to 700°C) and cold in capsules. In addition to measuring the gas production in the capsule tests, these

tests will be used to study the change in microstructure of the material irradiated hot and cold, and after postirradiation annealing. Material of large and small grain size will be studied, as well as the effect of crystal orientation.

Fig. 186. Braze Region in an Out-of-Pile Creep Test. The dark particles are a boride intermetallic compound. 250X.

Fig. 187. Braze Region from an In-Pile Creep Test. This region was at the in-pile end of an MTR test specimen. Notice the voids in and around the particles of the dark boride intermetallic compound. 250X.

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