Expansion of Copper upon Low-Temperature Deuteron Irradiation*†

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The increase in linear dimensions of a 99.999% copper foil upon deuteron irradiation was measured directly as a function of integrated flux. Two bombardments were made on the same specimen with integrated fluxes of $3.14\times10^{16} d/\text{cm}^2$ and $7.68\times10^{16} d/\text{cm}^2$, respectively. It was found in both runs that the specific change in length per incident deuteron per square centimeter was 3.8×10^{-21}. This value applies to an average deuteron energy of 8.5 Mev. Measurements of the thermal recovery of the irradiation-induced change in length were also made. If the stages of thermal recovery between the bombardment temperature and room temperature are designated as Stage I (70°K), Stage II (70–180°K), and Stage III (180–300°K), then the amount of recovery per stage is 64%, 6%, and 26%, respectively. The residual effect remaining at 300°K is 4% of the maximum effect. It is suggested that the defects introduced by the deuteron irradiation are Frenkel pairs and that thermal recovery proceeds by means of recombination of vacancies and interstitials between the bombardment temperature of 17° and 300°K.

I. INTRODUCTION

THE imperfections existing in crystalline solids greatly influence the properties of the crystals. There are many ways in which these imperfections may be studied, one of which involves the use of high-energy particle irradiation. This field of irradiation effects in solids offers an excellent opportunity for a study of particular crystal imperfections. Much has been learned regarding the properties of these defects; however, their precise nature is still not known.

One reason for this lack of detailed understanding is a result of the nature of most of the measurements which have been reported to date. These measurements have been largely concerned with changes in electrical resistance occurring upon bombardment and subsequent annealing. Unfortunately their interpretations have some ambiguities; a measurement of more direct interpretation would be desirable. The present paper reports such an experiment; it is a report of the volume change in Cu which occurs upon irradiation. To show how the present experiment is related to earlier studies, we will first review a few published facts about damage in Cu. Since excellent reviews of radiation damage exist in several places,[1] however, no large amount of data will be presented.

Irradiation effects generally fall into two categories, those occurring during bombardment and those associated with thermal recovery. Each gives useful information about the defects produced by the irradiation. The amount and type of bombardment and the temperature of irradiation determine the concentration of defects produced. The maximum concentration for a given irradiation dosage will be obtained if the temperature of irradiation is kept low enough so that thermal recovery does not occur. It appears that this can be done in copper only by irradiating it below 20°K. Then the bombardment and thermal recovery effects may be separated, thereby making the interpretations of the experimental results more straightforward.

The first irradiations of copper from which thermal recovery effects appeared to be almost entirely eliminated were electrical resistivity measurements carried out below 20°K by Cooper, Koehler, and Marx.[2] On the assumption that only Frenkel pairs were produced by the irradiation, these investigators obtained an estimate of the concentration of these defects for a given integrated flux. This estimate was smaller by a factor of about five than the estimate resulting from the use of the simple theory of Seitz and Koehler.[1] In their recovery data they showed that various annealing stages occurred. In the present paper these stages will be denoted as follows: Stage I: to 70°K, Stage II: 70°K–180°K, Stage III: 180°K–300°K. About half the resistivity change resulting from the irradiation annealed in Stage I while most of the remaining damage annealed in Stages II and III. A small residual effect remained at room temperature.

Measurements of the change in volume of copper upon deuteron irradiation were first performed at liquid nitrogen temperature by McDonell and Kierstead.[3] They observed a small volume increase upon irradiation and their thermal recovery data showed that only a small amount of annealing occurred between their bombardment temperature of 80°K and 400°K. Unfortunately their experiment suffered from constraints placed on the copper by the manner in which the irradiation was performed.

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† This work was supported by the U. S. Atomic Energy Commission.
‡ Now at International Business Machines, Poughkeepsie, New York.

[1] F. Seitz and J. S. Koehler, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 305; J. W. Glen, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 381; H. Brooks, *Annual Review of Nuclear Sciences* (Annual Reviews, Inc., Stanford, 1956), Vol. 6, p. 215; G. H. Kinchin and R. S. Pease, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 1.

[2] Cooper, Koehler, and Marx, Phys. Rev. **97**, 599 (1955).

[3] W. McDonell and H. A. Kierstead, Phys. Rev. **93**, 247 (1954); **98**, 1870 (1955); H. A. Kierstead, Phys. Rev. **98**, 245 (1955).

The first investigation of irradiation effects in copper resulting from deuteron bombardment below 20°K other than a resistivity measurement was that performed by Simmons and Balluffi.[4] These investigators measured the change in lattice parameter upon irradiation and subsequent thermal recovery. They observed a linear increase of lattice parameter with integrated flux and thermal recovery effects which paralleled those observed by Cooper *et al.*[2]

The experiment described in the present paper reports measurements of the length change induced in high purity copper at 17°K by deuteron irradiation. The specific length change was measured directly to a precision of 5%. It was demonstrated in two bombardments, one short and one somewhat longer, that the damage introduced was a linear function of the integrated deuteron flux. In addition the annealing processes between the bombardment temperature and room temperature were studied. Excellent agreement was obtained between the present experiment and Simmons and Balluffi's lattice parameter measurement both for the bombardment and thermal recovery data. Furthermore the length change recovery curve closely followed the resistivity recovery curve of Cooper *et al.* under similar irradiation conditions.

II. EXPERIMENTAL PROCEDURE

The actual measurement of the change in length was complicated by several factors. The specimens themselves were of necessity fragile because the short range in copper of the bombarding particles did not allow the use of massive samples. Furthermore, the specimens had to be held in vacuum near liquid helium temperature during the bombardment. Since the effect of strain upon defect production during irradiation and upon thermal recovery was not known, all measuring devices which might produce strains in the specimen could not be used. Finally, a method had to be developed which would measure precisely small length changes because the effect was expected to be very small.

Prior estimates had indicated that the maximum specific length change, $\Delta L/L$, after a week's bombardment at 15°K with 12-Mev deuterons from the University of Illinois cyclotron would be certainly no greater than 10^{-3}. To get high precision it was thought necessary to be able to measure a length change to about $\pm 2\times 10^{-5}$ cm. An optical technique was developed which would do this. It consisted simply of a microscope with a long working distance fitted with a Filar micrometer eyepiece.[5] The measurement of the change in length consisted of observing with this microscope the change in position of a point on the specimen relative to a fixed point on the specimen holder.

[4] R. O. Simmons and R. W. Balluffi, Atomic Energy Commission Technical Report No. 10 At (11–1)–182 (unpublished); R. O. Simmons, thesis, University of Illinois, 1957 (unpublished).

[5] Use of this microscope was originally suggested by Professor J. S. Koehler.

Two measurements of deuteron-induced length changes with specimens cooled to 15°K and 25°K were made with this instrument. These preliminary measurements determined the order of magnitude of the bombardment effect in copper, silver, and gold and gave some thermal recovery data. They also showed that this simple method of measurement had some disadvantages: namely, taking the measurements was very tedious, no permanent record was obtained, and bending of the foil due to the production of nonhomogeneous damage in the specimen could not be detected. These disadvantages were eliminated or measured in the experiment reported in the present investigation by attaching a camera to the microscope and recording the data on photographic plates. The details of this technique will be pointed out later.

The low-temperature irradiation was performed with the specimen cooled by a liquid helium cryostat described by Mapother and Witt.[6] Heat generated in the specimen was carried by conduction from its ends to a block in good thermal contact with the liquid helium Dewar. A vacuum was maintained in the cryostat by attaching to its bottom a brass container (which will be designated as the "sump"). The specimen mounting block extended down into this sump in the deuteron beam which entered the sump through a tube connected to the cyclotron.

It is imperative that the total flux of deuterons incident on the sample be known. This integrated flux was measured by stopping the collimated beam in an extension of the liquid nitrogen Dewar (see Fig. 1) and meas-

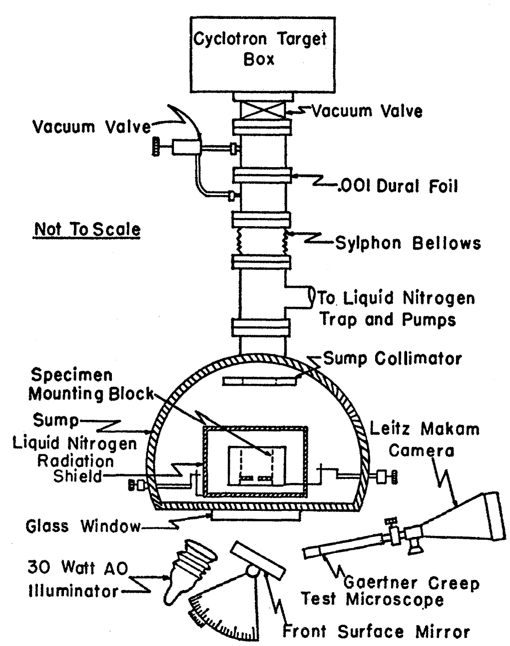

FIG. 1. Top view schematic diagram of apparatus.

[6] D. D. Mapother and F. E. L. Witt, Rev. Sci. Instr. 26, 843 (1955).

uring the accumulated charge. The liquid nitrogen and helium Dewars were electrically insulated from their stainless steel container and the attached sump. The charge that accumulated on the Faraday cage so constructed was then permitted to run through a current integrator which recorded the integrated deuteron flux as number of counts on a mechanical counter.[7]

In the final measurements two copper samples were irradiated. One was used for the length measurement while the second was merely a temperature monitor. Both were manufactured from American Smelting and Refining 99.999% pure copper rod, which was cold rolled from $\frac{1}{4}$ in. diameter to a strip 0.0034 in. thick. The purity of this copper was estimated from a measurement of its residual resistance. Two test samples were cut from it and annealed at about 500°C for 3 hours. The ratio of the room temperature resistance to the resistance at 4.2°K was then measured and found to be 1040 and 1080, respectively. If one assumes a resistivity of 1.5 μohm cm/*at.*% of impurity and a room temperature resistivity of 1.55 μohm cm, then the defect concentration is of the order of 10^{-5} (or the material is indeed 99.999% copper). The samples that were irradiated are believed to have this same purity.

The samples were made in the following manner. First they were cut into 4 cm$\times$2 mm strips and reduced in thickness to 0.0028 in. by a dilute HNO_3 etch followed by a $FeCl_3+HCl$ etch. The monitor foil was then bent down the middle into a rooftop shape in a stainless steel form to give it mechanical rigidity. The specimen on which the length measurements were made was cut in half and each half was similarly bent down the center in another stainless steel jig. With this jig a half-millimeter flattened portion was left on the end of each half to make optical observations easier. On these flattened ends fiduciary marks were made. First the end was chemically electropolished to smooth the surface and then light scratches were made with a razor blade. Finally the surface was electropolished again until it was almost smooth. The remaining surface irregularities produced high-contrast bright diffraction spots when viewed through the microscope. These spots were used as fiduciary marks.

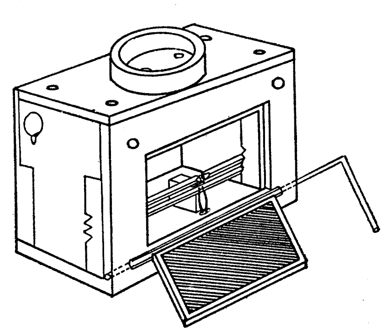

FIG. 2. Specimen mounting block.

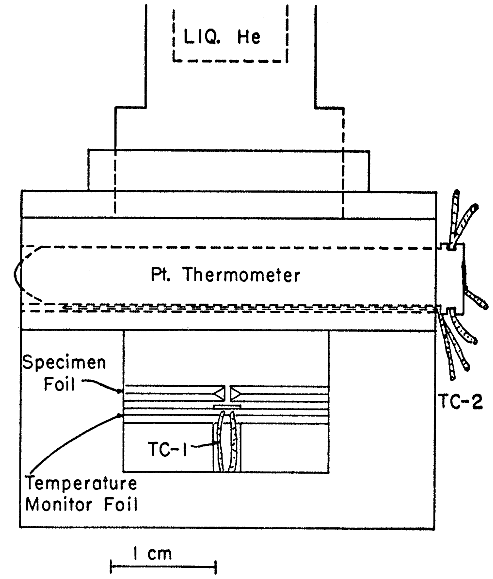

FIG. 3. Front view of specimen block. The thermocouples *TC*-1 and *TC*-2 and standard platinum resistance thermometer are shown.

The two specimen halves and the temperature monitor were mounted on a copper block by means of copper clamps at their ends as shown in Fig. 2. They therefore presented a 0.0039 in. projected thickness to the deuteron beam. The ends of the two halves of the specimen were separated by a gap of about 0.09 mm to allow for radiation expansion. The specimen was mounted in this way instead of using a single foil twice as long in order to increase the efficiency of cooling.

Since the temperature of the specimen foil itself cannot be measured, the monitor and specimen foils were placed side by side. See Fig. 3. A 0.005-in. copper and 0.010-in. constantan thermocouple was spot-welded to the center of the monitor foil. Possible radiation effects on the thermocouple were avoided by shielding it from deuteron irradiation with a thick copper stub. In this condition the block, specimens, and thermocouple were annealed in vacuum at about 350°C for six hours to remove the residual strains and improve the thermal conductivity of the block and foils. The thermal contact of the foil ends was further improved by the annealing since the copper clamp and foil sintered during this treatment. The block was then attached by screws to the stub on the liquid helium Dewar. At the interface of the block and Dewar a thin layer of varnish was used to insure good thermal contact.[8]

It was important to keep the specimen as cold as possible during the bombardment to prevent thermal annealing from occurring. In addition to providing good thermal contact to the helium Dewar it was necessary to take a number of precautions to reduce the heat flow

[7] H. T. Gittings, Jr., Rev. Sci. Instr. **20**, 325 (1949). A slightly modified version of the circuit described in this paper was used.

[8] It was found that a thin layer of G. E. 7031 varnish had excellent thermal conductivity at temperatures near 10°K.

from warmer parts of the cryostat to the specimen. Heat flow down the thermocouple wires to the junction was avoided by passing these wires through holes in the specimen mounting block before they were led outside the cryostat. Thermal radiation to the foils was considerably reduced by enclosing them in a radiation shield which was at the block temperature. The front and back parts of the shield through which the beam passed were made of copper foils 0.0005 in. in thickness. The front foil was part of a small door which could be opened manually during the length change measurement.

The temperature of the monitor foil was measured by means of the copper-constantan thermocouple attached to its center. A second similar thermocouple was used to measure the block temperature. These thermocouples were both calibrated in place prior to the bombardment against a standard platinum resistance thermometer.

The heat flow to the block occurred primarily by conduction down the thermocouple wires. Hence these wires were cooled to liquid nitrogen temperature before they were led to the block. In this way the liquid helium evaporation rate was reduced to 2.5 cu ft of gas/hour. During the irradiation, however, the rate increased by factors of 6 to 10 depending upon the deuteron beam current.

The vacuum required for the optical observation of a metallic surface at temperatures near that of liquid helium must be extremely clean. It is absolutely necessary to have a liquid nitrogen trap in the pumping system to keep oil vapors out of the cryostat vacuum system. Such oil vapors would condense on the cold specimens and obliterate the spots at low temperatures. In addition numerous dry runs in the laboratory showed large pressure bursts at several temperatures between 25°K and room temperature. These bursts were apparently caused by evolution of condensed gases from the cold metal surfaces when a particular phase transition point of one of the gases was reached in the warmup. At such transition points rather high pressures were produced in the vacuum system. At these temperatures there was so much condensation on the specimen that the fiduciary spots were obliterated. To prevent this loss of spots during a gas burst or as a result of slow condensation at 17°K it was necessary to keep the small door on the specimen block shut at all times except when measurements were being made. Furthermore, measurements could not be made during the gas bursts. In the cryostat used in the present investigation three pressure bursts occur upon warmup from helium temperature. They reached their maximum pressures during the warmups at block temperatures of about 35°K, 100°K, and 200°K. The first two of these are possibly caused by melting and boiling of oxygen which had condensed on parts of the helium Dewar. The gas burst at 200°K is probably caused by sublimation of CO_2.

A schematic drawing showing the location of the optical system relative to the specimen is also shown in Fig. 1. The heart of the measuring equipment is the microscope and camera. (The microscope was a Gaertner "creep test" microscope with a 5-in. working distance. The camera was a Leitz "Makam" camera with a specially designed cassette.)[9] The specimen was viewed in a front surface mirror through open doors on the block and nitrogen shield and through a glass window on the front of the sump. It was illuminated with a 30 watt *AO* illuminator fitted with a glass heat-absorbing filter. By using oblique illumination it was possible to make the spots appear bright against a dark background. Ten second exposures were made on $3\frac{1}{4}\times4\frac{1}{4}$-in. Kodak Metallographic plates. The heating effect of the illuminator when the block was at 12°K amounted to raising the temperature of the monitor by about one degree during the exposure of the plate. The natural vibration of the system was sufficiently damped by tying the helium Dewar to the nitrogen Dewar and wedging the latter against the sump with a piece of Tygon. Shrinkage of the emulsion was negligible but slight variations in magnification due to refocusing were corrected for in the analysis. Photographs of the specimen were taken at normal incidence; the equipment in this position was calibrated by a Leitz stage micrometer having 0.01 mm divisions.

The length data were read from photographic plates; a typical example is given in Fig. 4. The change in length showed itself by the motion of the spots on one foil relative to those on the other. This relative motion was measured with a Gaertner coordinate comparator. The length changes were computed from the motion of spots 3, 4, 5, and 6 on the right foil relative to spots 1 and 2 on the left foil. This was done by measuring the (x, y) coordinates of each of the six spots per plate. In order to introduce a common coordinate system on all the plates, it was necessary to perform a translation and rotation of the actual coordinate system introduced when the position of the spots on each plate was measured on the comparator. This was done by translating the origin of the existing coordinate system on each plate to spot No. 1 and then rotating it so that the "y" axis passed through spot No. 2. The new positions of the spots on each plate were calculated by means of the University

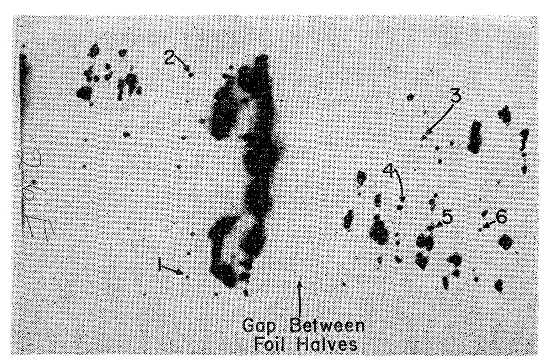

FIG. 4. One of the photographic plates.

[9] Use of this camera was suggested by Mr. T. Nilan.

of Illinois digital computer. Variations in magnification and thermal expansion among the plates were corrected for by taking a standard length on one of the specimen halves on a standard plate and insisting in the calculations that this distance by uniform on all plates. This was done by using the distance between spots No. 1 and No. 2, r_{12}^*, on a particular plate, say plate No. 1, as the standard length and then multiplying the translated and rotated coordinates of the spots on other plates as calculated above by the factor r_{12}^*/r_{12}, where r_{12} is the corresponding distance on the plate in question. The fact that r_{12} increased with irradiation is not significant since its maximum change was of the order of 9×10^{-6} cm. This change would introduce a similar change in the position of the spots and since this value was less than the experimental error, it could be neglected.

After all the foregoing calculations and corrections were made, a set of numbers was obtained for each spot on every plate. These numbers represented the coordinates of that spot relative to a fixed coordinate system (based on spots 1 and 2). These numbers could then be plotted for the spots 3, 4, 5, and 6, and from such plots the change in length at any time could be deduced.

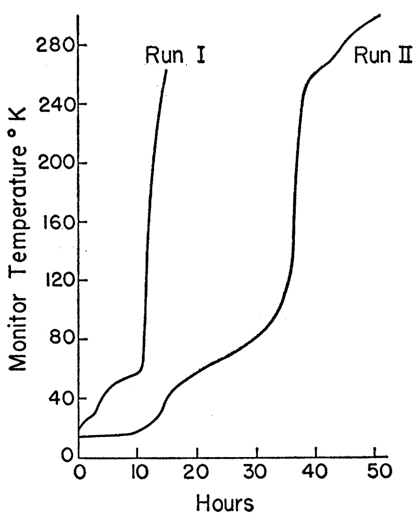

FIG. 5. Temperature of foil during warmup.

III. RESULTS

Measurements were made on two successive bombardments of the same specimen. The temperature of irradiation for both runs was 17°K. Run I had a final integrated flux of 3.14×10^{16} deuterons/cm^2 while Run II had a dosage of $7.68\times10^{16}d$/cm^2. After the irradiation in Run I, the specimen was warmed to 264°K before coolants were again added to the cryostat. The recovery of damage in Run I was essentially complete by 264°K since a residual length change in the specimen of only 2×10^{-5} cm remained. This value corresponds to the experimental error (at 264°K). The specimen was then cooled to 10°K and Run II was performed. When this irradiation was terminated, the specimen was warmed to a temperature of 293°K and the amount of thermal recovery was measured at this temperature and then checked at 7°K by adding coolants to the cryostat. At this time the residual length change was again 2×10^{-5} cm. The rates of warming for the two runs are given in Fig. 5.

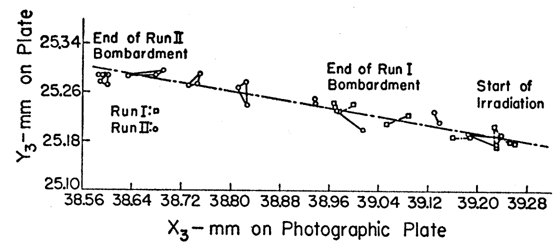

FIG. 6. Plot of part of the data from which expansion was determined. Two-dimensional spatial motion of spot No. 3 relative to spots No. 1 and 2 during Run I and Run II bombardment. The plane of the observed motion is the plane perpendicular to the deuteron beam. Each point represents the position of spot No. 3 as measured on a particular photographic plate. Straight lines join points corresponding to plates exposed at identical integrated fluxes.

The radiation expansion data were obtained from the two dimensional motion of spots 3, 4, 5, and 6 relative to 1 and 2 as explained in the previous section. In Fig. 6 this motion is shown for spot No. 3. (It is typical of the graphs of the motions of the other three spots.) Each point represents the position of spot No. 3 on a single photographic plate. The units used in the abscissa and ordinate are physical distances on the plate. The expanded condition of the foil was determined from the normal projections of the positions of the points on the line giving the direction of expansion. It will be noted that at the maximum expansion the foils are slightly distorted since the points tended to fall below the direction of the expansion. This distortion is even more pronounced on spatial plots of points 4, 5, and 6.

The curve shown in Fig. 7 was obtained by averaging

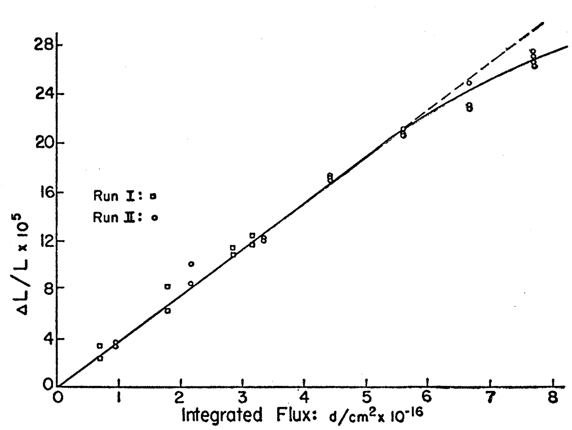

FIG. 7. Plot of bombardment curves showing radiation expansion. Each point represents the expansion observed as a result of the average change in positions of spots 3, 4, 5, and 6 relative to 1 and 2.

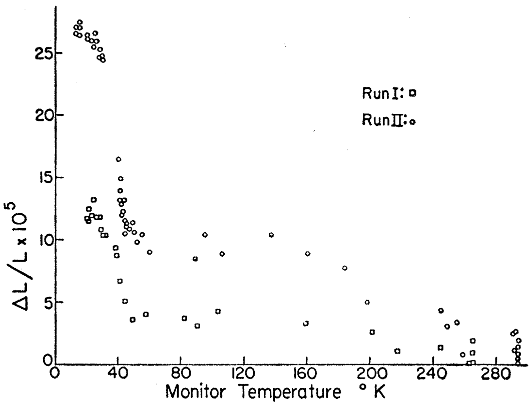

FIG. 8. Thermal recovery to room temperature. Each point represents the average residual $\Delta L/L$.

the radiation expansion observed as a result of the motion of spots 3, 4, 5, and 6 relative to 1 and 2. Each point in this figure is the mean value of the relative motion of the 4 spots per plate used to determine the expansion. It will be seen that the slopes of the two bombardment curves for Runs I and II are the same within the experimental error. The average value of the specific change in length per deuteron per cm² was found to be

$$\frac{\Delta L/L}{d/\text{cm}^2} = (3.8\pm0.2)\times10^{-21}.$$

This value applies to an average deuteron energy of 8.5 Mev.

During thermal recovery the spatial motion of the spots was the reverse of that occurring during expansion; the average data are plotted in Fig. 8. Because of the smaller effect in Run I, the precision was not as good in it as in Run II, nevertheless, the recovery data of both runs agree in all their aspects within the experimental error. For the sake of simplicity the thermal recovery regions may be designated as follows: Stage I, specimen temperature less than 70°K; Stage II, 70°K to 180°K; and Stage III, 180°K to 300°K. The thermal recovery occurring in Stage I is plotted in Fig. 9 on a greatly expanded scale. In Run II Stage I recovery accounted for 64% of the damage, Stage II accounted for 6%, and Stage III accounted for 26%, leaving about 4% at room temperature. The residual effect after Run II can be compared with the total effect of irradiation in both Runs I and II. Therefore the amount of damage remaining after a total irradiation of $10.8\times10^{16} d/\text{cm}^2$ (which would produce a total length change of about 76.8×10^{-5} cm) is about 4×10^{-5} cm or about 5% of the effect. This value is about twice the experimental error in measuring the length and therefore represents a small but real residual effect.

Although sufficiently precise measurements of the change in thermal conductivity were not made, it was however noted that a cumulative decrease resulted from increasing irradiation dosage. This decrease in thermal conductivity at the bombardment temperature of 17°K was found to anneal out upon warming to 20°C.

IV. DISCUSSION

1. Radiation Expansion

It is desirable that an irradiation designed to produce measurable changes in the physical properties of a metal be carried out at a temperature where thermal recovery does not occur. Various investigators have reported the start of low temperature annealing somewhere in the vicinity of 15° to 21°K.[2,4,10] In the present investigation the maximum bombardment temperature was 17°K and annealing was observed to commence very slowly between 18° and 20°K. Hence it does not appear likely that appreciable thermal recovery occurred during the irradiation.

The first observation that can be made is that the radiation expansion was positive. Calculations have shown that the volume increase due to an interstitial atom in the lattice is roughly five times the volume decrease due to a vacancy.[11–17] Hence the above result is in agreement with the assumption that Frenkel pairs are produced by the irradiation.

It is also interesting to compare the radiation expansion of the present investigation with the lattice parameter change observed by Simmons and Balluffi.[4] The experimental conditions in both experiments were very similar, the only correction needed to compare them is that due to the $1/E$ energy dependence of damage ob-

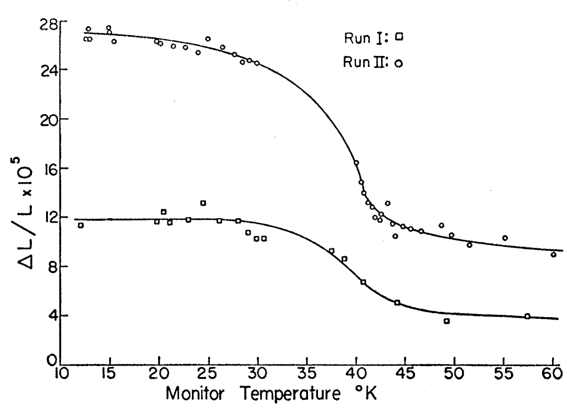

FIG. 9. Thermal recovery in Stage I.

[10] Corbett, Denney, Fiske, and Walker, Phys. Rev. **104**, 851 (1956).
[11] H. B. Huntington, Phys. Rev. **91**, 1092 (1953); Acta Met. **2**, 554 (1954).
[12] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).
[13] G. J. Dienes, Phys. Rev. **86**, 228 (1952).
[14] C. W. Tucker, Jr., and J. B. Sampson, Acta Met. **2**, 433 (1954).
[15] J. B. Sampson and C. W. Tucker, Jr., Phys. Rev. **105**, 1117 (1957).
[16] J. Eshelby, J. Appl. Phys. **25**, 255 (1954); *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 79.
[17] Ludwig Tewordt (to be published).

served by Simmons and Balluffi. In the present investigation the average value of the deuteron energy was 8.5 Mev while in Simmons and Balluffi's measurement a value of about 7 Mev applied. The value of the specific lattice parameter change per deuteron per square centimeter, $(\Delta a/a)/(d/\text{cm}^2)$, for 7-Mev deuterons was found by them to be $4.1\times10^{-21}/(d/\text{cm}^2)$. This value corrected to an energy of 8.5 Mev is $3.4\times10^{-21}/(d/\text{cm}^2)$. The value of the specific length change per deuteron per square centimeter, $(\Delta L/L)/(d/\text{cm}^2)$, observed in the present experiment is $3.8\times10^{-21}/(d/\text{cm}^2)$. These two results differ by 11% and show that the $1/E$ energy dependence of damage is verified to at least this precision. One can also conclude that $\Delta a/a=\Delta L/L$ to a precision of 11%. It should be pointed out in this connection that Simmons and Balluffi's bombardment temperature was about 5 degrees below the 17°K bombardment temperature of the present investigation. While it is possible that the resulting damage in the two cases could be different, it appears unlikely that this should be the case.

It is also useful to compare the change in resistivity to the specific length change upon irradiation. This can be done by calculating the quantity $\Delta\rho/(\Delta L/L)$, where $\Delta\rho$ is the change in resistivity and $\Delta L/L$ is the specific length change upon irradiation. Using the initial slope of $2.3\times10^{-18}\mu$ohm cm$/(d/\text{cm}^2)$ for Cooper's resistivity damage curve[2] and making the energy correction from 9.5 Mev to 8.5-Mev deuterons, one gets a slope of $2.58\times10^{-18}\mu$ohm cm$/(d/\text{cm}^2)$. This value together with the length change data of the present investigation gives

$$\frac{\Delta\rho}{(\Delta L/L)}=6.8\times10^{-4}\text{ ohm cm.} \tag{1}$$

The value obtained for the same quantity using the lattice parameter data of Simmons and Balluffi's experiment is

$$\frac{\Delta\rho}{(\Delta a/a)}=7.6\times10^{-4}\text{ ohm cm.} \tag{2}$$

As was noted earlier in this paper the existence of foil distortion was clearly evident near the maximum integrated fluxes used in the irradiation. This distortion is probably the result of the production of inhomogeneous damage in the specimen caused both by the $1/E$ dependence of damage through the specimen thickness and by a possible nonuniform deuteron beam across the face of the specimen.

No evidence of any "radiation annealing" was observed in the present irradiation at least up to an integrated flux of $6\times10^{16}d/\text{cm}^2$. Beyond this value the distortion of the foil has masked any such effect.

2. Thermal Recovery

The thermal recovery of the bulk expansion was similar to that noted earlier for recovery of both resistivity and lattice parameter.[2,4] A comparison of the recovery of these three properties is shown in Fig. 10. In general the agreement among all three recovery curves is very good, but the agreement between the residual lattice parameter change and radiation expansion is indeed excellent. The relative amounts of resistivity, lattice parameter, and length change remaining after Stages I (<70°K), II (70°K–180°K), and III (180°K–300°K) of recovery are shown in Table I. While the choice of temperature limits for the three recovery stages is somewhat arbitrary, it is believed nevertheless that a reasonable choice has been made. It appears that if radiation annealing had not occurred in the measurement of the resistivity change upon irradiation, then the agreement would be considerably better.

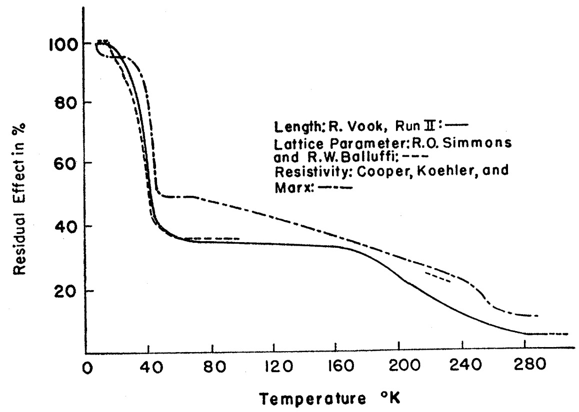

FIG. 10. Comparison of low-temperature recovery effects of resistivity, lattice parameter, and macroscopic length.

3. Effect of Impurities and Other Crystal Imperfections

It is possible that small concentrations of impurities might affect the thermal recovery of copper. The estimated impurity concentrations for the specimens used in the resistivity measurements of Cooper *et al.*,[2] the lattice parameter measurements of Simmons and Balluffi,[4] and the present investigation were 3×10^{-4}, 3.5×10^{-5}, and 1.0×10^{-5} impurity atoms/lattice atom, respectively. The variation by a factor of 30 in the impurity concentration shows that impurities have little effect on annealing properties, at least for these small concentrations, since the recovery curves for all three properties are very similar. This is in agreement with

TABLE I. The relative amounts of resistivity, lattice parameter, and length change, remaining after the various stages of recovery.

	$\Delta\rho/\Delta\rho_{Max}$ remaining	$\Delta a/\Delta a_{Max}$ remaining	$\Delta L/\Delta L_{Max}$ remaining Run II
Stage I	50%	37%	36%
Stage II	33%		30%
Stage III	10%	4%	4%

the data of Blewitt who found that for neutron irradiation, significant effects were not observed for impurity concentrations less than 1×10^{-3}.[18]

Grain boundaries appear to have little effect on radiation expansion and its recovery. The polycrystalline specimens used in the present investigation had grains smaller than the specimen thickness, while the copper single crystal used by Simmons and Balluffi for their lattice parameter measurements gave essentially the same results as those reported in this paper.

4. Interpretation

Several types of defects have been suggested as being responsible for the effects occurring during irradiation. For comparison of experiment with various theoretical calculations it will be assumed that the defects produced during low-temperature deuteron irradiation are Frenkel pairs. Although this assumption is made somewhat arbitrarily, it appears to be the best that can presently be made. On this basis then, the results of this investigation will be compared with properties which have been calculated for Frenkel pairs.

The first comparison to be made between theory and experiment is that of the number of defects produced during irradiation. To compute this number from the experimentally determined length change, one uses the linear expression

$$\Delta L/L = Af,$$

where $\Delta L/L$ is the specific length change per deutron per square centimeter, f is the fraction of atoms displaced per d/cm^2, and A is a constant. A is presently not known accurately; a range of values of A between 0.15 and 1.0 has been calculated.[11–17] A recent calculation by Tewordt gives a value for A lying near the middle of this range, namely $A=0.5$.[17] Use of this number to calculate f from the present experiment yields $f=7.6\times10^{-21}$ per incident deuteron/cm². The specimens contained about 8.4×10^{20} atoms/cm², so the number of displaced atoms per incident 10.7 Mev deuteron is 6.4.

The simple theory of Seitz and Koehler[1] can be used to predict the concentration of defects which should be produced by the incident deuterons. Such a calculation gives $f=4.8\times10^{-20}$ per incident deuteron/cm²; so the predicted number of displaced atoms per incident deuteron is 40.5. This number is 6.3 times higher than that computed from the experimental data. Smaller values of the constant A would make this agreement better, but it is unlikely that it could be reduced enough to make the agreement satisfactory. One must therefore conclude that the simple theory overestimates the number of defects produced.

It was noted earlier that to within 11% the observed x-ray expansion was equal to the bulk linear expansion. The damage for both these measurements varied by about 40% from the front to the back face of the specimen. However, the short penetration depth of the x-rays in the former experiment and the favorable geometry in the latter permitted a comparison of the two results. The variation of inhomogeneity of damage in the small x-ray penetration depth was no more than a few percent. Calculations were made which showed that the effect of inhomogeneity on the measurement of the average bulk linear expansion was also at most of the order of a few percent. Hence upon adding up the experimental and known systematic errors it appears that the two experiments ought to agree to within 20%. As was shown in this paper, the actual agreement is 11%.

The resistivity of Frenkel pairs in copper can be readily calculated using the resistivity changes observed by Cooper *et al.*[2] and the data of the present experiment. Their initial resistivity change per incident deuteron per cm² was about $2.58\times10^{-18}\mu$ohm cm/(d/cm²) when corrected to a deuteron energy of 8.5 Mev. From the present experiment one has $f=7.6\times10^{-21}$ per incident deuteron/cm². The resistivity per atomic percent of Frenkel pairs is then 3.4μohm cm. This value is intermediate in the range estimated from theory and other experiments for this number; estimates have ranged between 0.75 μohm cm and 12 μohm cm.[19–23]

The annealing of the radiation expansion also may be used to make some observations about the defects produced. Again the statements which can be made are strengthened by considering the bulk expansion along with the x-ray lattice expansion measurements and the measurements of electrical resistance. Two general observations can be made.

(1) Where comparison is possible during thermal recovery, the fractional amount of ΔL and Δa remaining at a particular temperature, $\Delta L/\Delta L_{\max}$ and $\Delta a/\Delta a_{\max}$, are equal to within 5%. The only exception occurs at 227°K where the single point of the residual $\Delta a/\Delta a_{\max}$ at that temperature differs from the residual $\Delta L/\Delta L_{\max}$ curve by slightly less than 10%. The fact that about equal fractions of resistivity, lattice parameter and length change are left after annealing to specific temperatures in the region below 300°K suggests that recombination of vacancies and interstitials occurs throughout this temperature range. Actually a good comparison cannot be made between 90°K and 300°K because of insufficient lattice parameter data.

(2) From the present experiment an estimate can be made of the energy which should be released in the thermal recovery. This estimate will be based on the assumptions that only Frenkel pairs are produced during the irradiation and that these are annihilated in thermal recovery. Furthermore it will be supposed that the energy of formation of a Frenkel pair is 5 ev. Using these assumptions one finds that the energy released

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[18] Blewitt, Coltman, Klabunde, and Noggle, J. Appl. Phys. **28**, 639 (1957).

[19] P. Jongenburger, Phys. Rev. **90**, 710 (1953); Appl. Sci. Research, Sec. B. **3**, 237 (1953); Nature (London) **175**, 545 (1955).

[20] F. Blatt, Phys. Rev. **99**, 1708 (1955).

[21] D. L. Dexter, Phys. Rev. **87**, 768 (1952).

[22] A. W. Overhauser and R. L. Gorman, Phys. Rev. **102**, 676 (1956).

[23] Walter Harrison (to be published).

during the complete thermal recovery of the copper specimen used in Run II should be about 1.1 cal/g.[24] This energy release when normalized to a 1 μohm cm resistivity change (using Cooper's initial resistivity change per $d/\text{cm}^2)^2$ is 5.4 (cal/g)/μohm cm. The only measurement of stored energy on deuteron irradiated samples was performed by Overhauser.[25] He found that between liquid nitrogen temperature and room temperature the stored energy release was 1.7 (cal/g)/μohm cm. No measurements on deuteron irradiated samples have been made below liquid nitrogen temperature. The only measurement of stored energy in copper below liquid nitrogen temperature was performed by Blewitt, Coltman, Holmes, and Noggle on neutron irradiated samples.[26] Their measurement indicates that the stored energy was less than 0.8 (cal/g)/μohm cm in the temperature range between 22°K and 60°K. It is clear that this value of stored energy is considerably smaller than the value predicted above. Since it is possible that the damage resulting from neutron irradiation is different from that produced by deuteron irradiation, a measurement of the energy released in Stage I recovery for the latter case should be performed. If the same result obtains for deuteron irradiation it appears that annihilation would not be the dominant process occurring in Stage I recovery.

[24] This value corresponds to an energy decrease of about 4.3 Mev from an incident deuteron energy of 10.7 Mev to 6.4 Mev.

[25] A. W. Overhauser, Phys. Rev. **94**, 1951 (1954).

[26] Coltman, Blewitt, and Noggle, Rev. Sci. Instr. **28**, 375 (1957); Blewitt, Coltman, Holmes, and Noggle, *Creep and Recovery* (American Society of Metals, Cleveland, 1957), p. 84.

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Ionization Rates for Electrons and Holes in Silicon

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The ionization rates for holes and electrons in silicon have been determined over the following ranges of field: for holes, $(2.5\text{–}6.0)\times10^5$ volts cm^{-1}; for electrons, $(2.0\text{–}5.0)\times10^5$ volts cm^{-1}. The ionization rate for electrons is higher than that for holes. The results suggest that the field dependence of the ionization rate for holes and, probably, for electrons also, can be expressed by $a\exp(-b/E)$, where E is the field. The constants a and b are different for electrons and holes.

INTRODUCTION

The charge multiplication that results when carriers are injected into silicon *p-n* junctions was measured as a function of the reverse bias by McKay and McAfee[1,2] and explained as an avalanche process similar to that used by Townsend as a mechanism for breakdown in gases. Making the assumption that the ionization rates for holes and electrons were equal, McKay was able to deduce the field dependence of the ionization rate. More recently, by fitting empirical relations to the multiplication *versus* bias measurements, Miller[3] has been able to solve the analytical expressions for the multiplication for the case where the ionization rates for holes and electrons are different. Miller's results were confined to fields greater than 4×10^5 volts cm^{-1}.

By using more refined methods for measuring the multiplication as a function of bias, the ionization rates have now been determined over a very much wider range of fields for a given junction. In particular, it has proved possible to obtain the separate ionization rates for holes and electrons rigorously, that is, without having to use empirical relations of somewhat limited validity. The results reveal an interesting relation for the field dependence of the ionization rate.

[1] K. G. McKay and K. B. McAfee, Phys. Rev. **91**, 1079 (1953).

[2] K. G. McKay, Phys. Rev. **94**, 877 (1954).

[3] S. L. Miller, Phys. Rev. **105**, 1246 (1957).

EXPERIMENTAL

The technique used to determine the multiplication characteristics down to multiplications of 1.001 has been described elsewhere.[4] The charge multiplication, M, produced by carriers injected into a *p-n* junction was measured as a function of the reverse bias, V, for two different grown junctions. The high-resistivity side of junction A was n type while that of junction B was p type. The position of the light beam relative to the junction was adjusted so as to produce a maximum signal with zero or low reverse bias applied. Thus, the

[4] A. G. Chynoweth and K. G. McKay, Phys. Rev. **108**, 29 (1957).

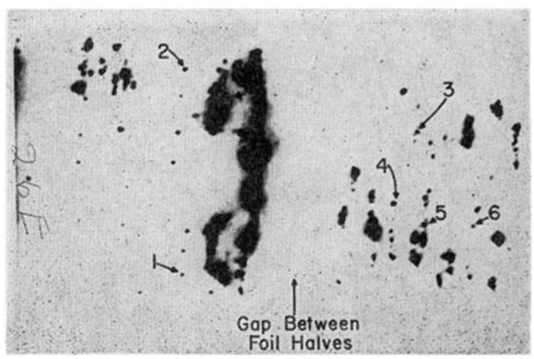

FIG. 4. One of the photographic plates.