Irradiation Effects in Cu, Ag, and Au Near 10°K*

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Electrical resistivity increases produced by 12-Mev deuteron irradiation were measured as a function of integrated deuteron flux in Cu, Ag, and Au. The bombardment temperature was near 10°K and no thermal recovery of the irradiation effects was observed; however, evidence that appreciable radiation annealing occurred during the bombardment was found. The resistivity increases near 10°K were much larger than those previously obtained in these metals for equal irradiations made near liquid nitrogen temperature. The observed Z-dependence of the irradiation effects agreed closely with that predicted by Seitz's theory.

Warmups made following the bombardments revealed that 40 to 50 percent of the total resistivity increase in Cu recovers near 43°K and from 13 to 24 percent of that in Ag anneals near 30°K; the rapid recovery in each case indicates that a unique process may be involved, and the associated activation energy is estimated to be 0.1 ev for both. It is suggested that volume diffusion of interstitial atoms or annihilation of very close interstitial atom-vacancy pairs are two possible processes responsible for the low temperature recovery. In addition, for all three metals, a gradual annealing rate was observed in the intermediate temperature range 50°K–220°K, and then a more rapid rate took place in the range 220°–280°K.

I. INTRODUCTION

FAST particle irradiation of metals introduces lattice defects which are believed to be largely equal concentrations of interstitial atoms and vacancies.[1] Although many physical properties of the metals are altered by the presence of such imperfections, electrical resistivity changes have extensively been used for their study since this property is both sensitive to small defect concentrations and easily measured experimentally. Previous work[2–4] on Cu, Ag, and Au, irradiated near liquid nitrogen temperature, has shown that most of the resulting increases in resistivity anneal out below room temperature and that considerable thermal recovery still occurs at temperatures as low as −180°C. For these basic studies it would be highly desirable that all of the imperfections created by the bombardment be "frozen in," since it is possible that new types may be observed, and in addition, it should then be possible to unambiguously decide whether radiation annealing, due to collisions of the fast particles with the lattice, is important. When thermal and radiation recovery simultaneously occur during the bombardment, it is difficult to separate the two types of annealing since they both cause a decrease in resistivity. All of the above experiments were performed near liquid nitrogen temperature, hence it is evident that bombardments using liquid hydrogen or helium as a coolant are necessary for further reduction or total exclusion of the thermally activated processes.

In the present investigation,[5] pure wires of Cu, Ag, and Au were mounted on a liquid helium cryostat and irradiated by 12-Mev deuterons from the University of Illinois cyclotron. The choice of these three metals was made for the following reasons: the results of previous theoretical work and the above mentioned experimental studies on them were available, high purity specimens of each could readily be obtained, and their similar electronic structure permitted Z-dependence estimates of the irradiation effects. Changes in resistivity were measured during the bombardment and the recovery was followed as the cryostat subsequently warmed to room temperature.

II. SAMPLE DESIGN AND MOUNTING

Samples in the form of 5-mil diameter Cu and Ag and 4-mil diameter Au wires were used. Wires were selected, rather than foils, in order to reduce the specimen area exposed to the beam and thus lower the liquid helium consumption. The sizes were chosen such that the diameter of each was about 60 percent of the 12-Mev deuteron range in that material. In this region the rate of deuteron energy loss $(dE/dx)_{\text{displ}}$, due to the displacement of atoms, is essentially constant;[1] and hence a desirable homogeneity of defects throughout the irradiated portion of the metal wires is approximately produced.

Special design of the specimens and their holder was necessary since a Wheatstone bridge circuit, similar to one previously used in this laboratory by Overhauser,[3] was employed for the resistivity measurements. This method permitted the thermal part of the irradiated specimen's resistance to be cancelled out by placing, in an opposite leg of the bridge, an equal but unbombarded specimen of the same metal. This circuit is shown in Fig. 3 and will be discussed further in the next section.

The required two identical samples were made by

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[1] F. Seitz, Discussions Faraday Soc. **5**, 271 (1949).
[2] Marx, Cooper, and Henderson, Phys. Rev. **88**, 106 (1952).
[3] A. W. Overhauser, Phys. Rev. **90**, 393 (1953).
[4] R. R. Eggleston, Acta Metallurgica **1**, 679 (1953).

[5] Preliminary results of this experiment were reported in Phys. Rev. **94**, 496 (1954).

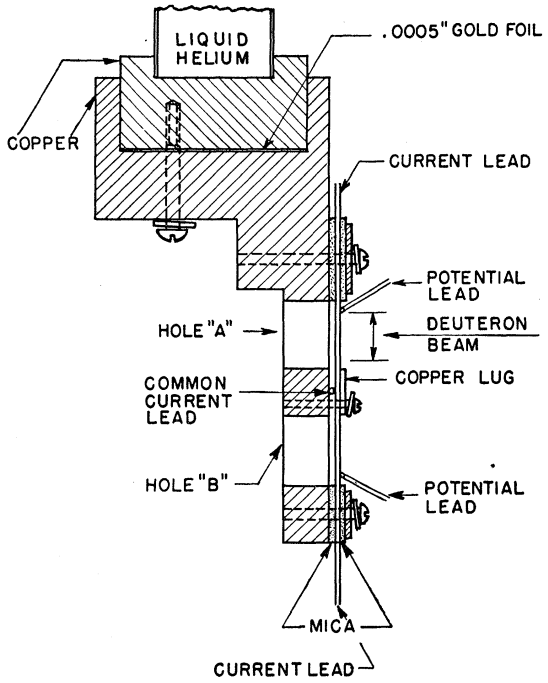

FIG. 1. Target block and specimen mounting.

accurately spot welding three copper leads, equally spaced $\frac{7}{16}$ inch apart, at right angles to a four inch length of pure specimen wire. The center welded contact, which was a 10-mil copper wire, served as a common current lead to the two equal sections of the sample; and the other two, consisting of 3-mil copper wire, were utilized as potential leads. With the aid of a Lucite jig for the spot welding operation, the two halves of each specimen were balanced to within one percent of the single section resistance.

The problem of mounting the specimens such that they are properly cooled, and at the same time insulated for resistance measurements, has been among the more difficult ones that arise in an experiment of this nature. Immersion of the specimens in the coolant was precluded by the short range of the 12-Mev deuterons (8 mils in Cu). A rather satisfactory solution was obtained by mounting the balanced specimens, as shown in Fig. 1, on a copper target block which was in contact with liquid helium. The 10-mil common current lead was fastened directly against the block with a copper lug, thus insuring good thermal contact to the specimens. The two ends of the specimen were clamped between mica sheets of 0.5-mil thickness with copper bars. The thin mica provided electrical insulation necessary for resistance measurements, and in addition it permitted a moderate thermal connection between the copper block and the ends of the samples. The 3-mil potential wires were similarly insulated and clamped on either side of the target block for the twofold purpose of preventing excessive strains at the spot weld joints and reducing heat conduction to the specimens through these leads.

Since it would be very wasteful of liquid helium if the energy of the entire deuteron beam were dissipated on the target block, the hole "*A*" was cut so that all of the beam could pass through the block. Hence only the small portion of beam energy lost in traversing the thin wire specimens was expended to liquid helium and the remainder was absorbed at a liquid nitrogen cooled radiation shield. For subsequent annealing studies, identical mounting of the matched specimens was desired, thus hole "*B*" was placed adjacent to the unbombarded sections and was made the same size as hole "*A*."

III. EXPERIMENTAL PROCEDURE

The polycrystalline specimens, which had a purity of 99.97 ± 0.02 percent, were mounted as described above and the complete assembly was then annealed for three hours at 400°C in a 10^{-5} mm of Hg vacuum. With a 0.5-mil gold foil at the interface for good thermal contact, the target block was bolted to the base of a spherical liquid helium flask in a metal cryostat especially designed for irradiation studies.[6] The lower section of the cryostat and beam tube arrangement are shown in Fig. 2. A copper cylinder, cooled by liquid nitrogen, shielded the target block from thermal radiation and also served as a Faraday cage for collection of the charged deuterons and secondary electrons. The grounded collimator No. 1 defined the area of the beam entering the Faraday cage; this beam was then further reduced in cross section by collimator No. 2, which accurately aligned it to hole "*A*" in the target block. A 0.5-mil copper foil, placed over the No. 2 aperature, prevented admission of thermal radiation. Electrical leads for resistivity and temperature measurements were brought in the top of the cryostat through Kovar seals. A P.I.G. gauge mounted on the outer cryostat wall indicated that the vacuum inside the cryostat was maintained near 10^{-5} mm of Hg during the bombardments. The liquid helium evaporation rate,

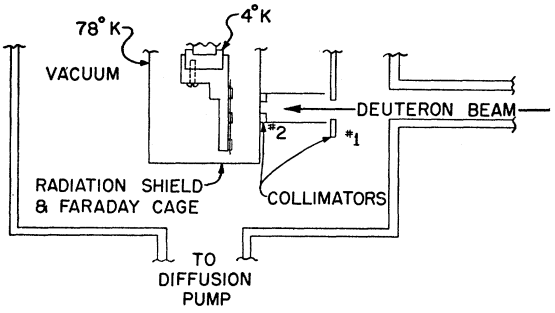

FIG. 2. Diagram of target block, radiation shield, collimators, and cyclotron beam tube assembly.

[6] A detailed description of this cryostat will be given by D. E. Mapother and co-workers in a future edition of *The Review of Scientific Instruments*.

which varied between 2.5 and 4.0 liters per day, was monitored by a gas flow meter connected in series with the helium flask exhaust tube.

The deuteron flux was recorded by insulating the entire inner part of the cryostat from the cyclotron ground, with a Teflon gasket, and then passing the charge collected on the Faraday cage through an electronic current integrator. The homogeneity of the beam distribution was determined from five copper monitor wires placed in the beam near the specimens. The radioactive Zn^{65} induced in these wires was counted and found to be constant, within 10 percent, over the beam area $\frac{3}{4}$ inch wide by $\frac{1}{4}$ inch high that was used.

Two experiments were performed, denoted as Run I and Run II, with the duration of the bombardments being seven and five days, respectively. Throughout these periods the specimens were maintained at 10°K $\pm$2°K for Run I and 12°K$\pm$2°K for Run II, as determined from a copper-constantan thermocouple on the target block and correlation of the unbombarded specimen's resistance values to the Gruneisen function. The deuteron beam intensity had to be kept below 0.05 microampere per cm^2 at all times to avert excessive heating of the specimens.

At various intervals during the irradiations the beam was turned off, and resistance measurements were made with the circuit shown in Fig. 3. When switch S_1 was in position 2, as drawn, the two initially balanced halves of the sample, labeled R_b for the bombarded half and R_d for the dummy part, were incorporated as two legs of a bridge. The other two sections each consisted of 50 ohm precision resistors and maintained essentially equal currents in the two parallel branches at all times during the irradiation, since R_b never exceeded 3×10^{-3} ohm and R_d was about 10^{-4} ohm for all specimens. The single branch current was determined from the emf across a standard 1-ohm resistor, which was read

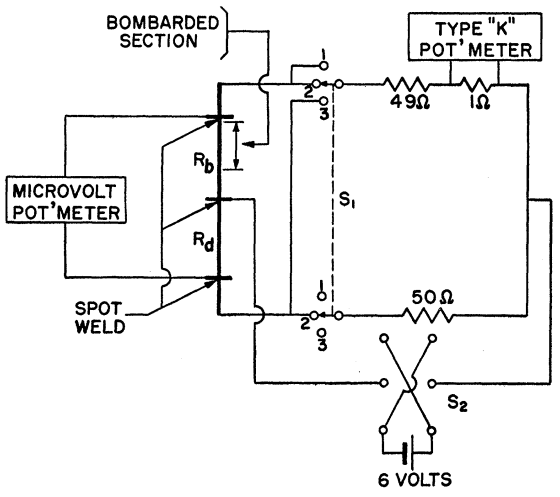

FIG. 3. Schematic diagram of circuit used for the resistance measurements. The matched bombarded and dummy specimens are R_b and R_d respectively.

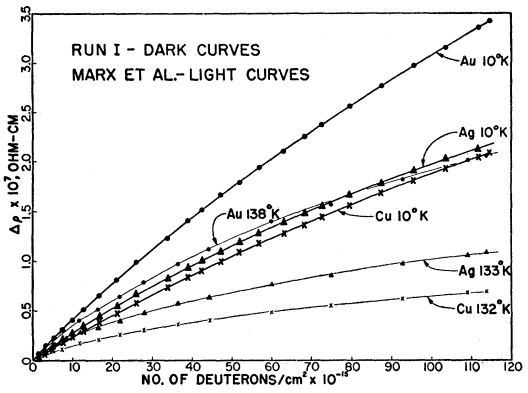

FIG. 4. Resistivity increase as a function of integrated deuteron flux—Run I and, for comparison, previous data obtained near 135°K by Marx *et al.* (See reference 2.)

on a Leeds and Northrup type K potentiometer. The off-balance voltage between the two potential leads was measured by a Rubicon Cat. No. 2766 thermofree microvolt potentiometer to an accuracy of $\pm5\times10^{-8}$ volt. Errors due to stray thermal voltages in the potential leads were eliminated by reversing the current through the bridge, with switch S_2, and taking the average of the readings for the two current directions. Simultaneous current and bridge voltage measurements made in this fashion yielded the resistance difference between R_b and R_d to a precision of 1×10^{-6} ohm, which was about 0.1 percent of the maximum difference. By switching S_1 to position 1, current was passed through the bombarded specimen only and R_b was measured directly using the standard potentiometric technique. Resistance changes obtained by this method were identical to the bridge values, within the experimental accuracy, and thus established confidence in the bridge method. The geometric conversion factor from resistance to resistivity, A/L, was determined from the ratio ρ_0/R_0 for the three metals, where ρ_0 is the handbook resistivity value at 0°C and R_0 is the measured specimen resistance at 0°C prior to irradiation.

After termination of the bombardments, the annealing of the defects was studied as the coolants ran out and the target block slowly warmed to room temperature. The warmup rate was usually in the range 15°K–30°K per hour. The bridge technique previously described was specifically designed for these studies, since it allowed the troublesome thermal resistance changes of the irradiated specimens to be balanced out. Simultaneous readings of the current, bridge voltage, and target block temperature were made for the specimens at frequent intervals during the warmup from 10°K to 300°K. Since it was not possible to match the bombarded and dummy specimens exactly, corrections for small resistance and temperature differences were determined from a similar warmup made before the irradiation and another following the annealing warmup. The average corrections from the latter two warmups

were taken, and subtracted from the appropriate measured values of the annealing warmup; thus yielding the desired net resistivity increase left in the bombarded specimen as a function of the annealing temperature.

In addition, at temperature intervals of about 10°K, resistance measurements of R_d for all samples were made potentiometrically by switching S_2 to position 3 in the circuit of Fig. 3. The temperature of the specimens at each of these points was then obtained by fitting these resistance values to the Gruneisen function. Substantial agreement, usually within 1°K, with the copper-constantan thermocouple attached to the target block was found.

IV. EXPERIMENTAL RESULTS

The plots of resistivity increase *versus* deuteron flux for Cu, Ag, and Au, that were obtained during Run I, are given by the dark curves of Fig. 4. These are to be compared with previous results of Marx *et al.*,[2] shown by the light curves on this figure, where the bombardment temperature was near that of liquid nitrogen. The initial slope of the 10°K curves are about a factor of two larger, for all three metals, than those of the liquid nitrogen curves; indicating that a considerable number of defects recover immediately in the latter case. The annealing curves that are shown later will shed some light on the nature of these recoveries.

A second experiment, Run II, was made for the purpose of checking the results of Run I and, in addition, to improve the annealing data. In this case the specimen temperatures were about 2°K higher than those of Run I, as a result of poorer thermal contact between the block and helium flask. The bombardment curves obtained from this run are shown in Fig. 5. Although the temperature difference between the two runs was small, the points on the Run II curves lie slightly below those of Run I for all metals and the percentage deviation becomes larger at higher deuteron fluxes. Figure 6 shows a comparison of the two curves for Cu, which is typical for the three metals. These differences would seem to indicate that thermal annealing was occurring at these low temperatures. However, after the end of the bombardments the specimens were held at or below (as much as 4°K) the irradiation temperature for 40 hours in Run I and 6 hours in Run II; with the result that no thermal recovery was observed, within the experimental accuracy of 0.1 percent. It then appears that this annealing must be due to collisions of the fast deuterons with the lattice; possibly in the form of thermal spikes, as originally suggested by Billington and Siegel.[7] The slightly higher ambient temperature of Run II would allow a higher absolute temperature to be reached in the vicinity of collisions, and hence result in more recovery for the second run. Table I contains a summary of the bombardment data for both runs.

The annealing curves obtained during Run I, as the specimens warmed to room temperature, are shown in Fig. 7. Unfortunately, a copious amount of deuterium had condensed on the liquid helium flask and created a gas burst in the cryostat during the very first part of the warmup. In turn, the ensuing pressure rise in the vacuum chamber produced a temperature pulse in the target block, the effects of which are indicated by the dashed lines on Fig. 7, because of increased thermal contact to the surroundings. The block went as high as 70°K and reached equilibrium at 27°K, as the deuterium was pumped out. Consequently, the data is not accurate at very low temperatures, but some conclusions may be made. Near 40°K a sharp drop of $\Delta\rho$ occurs in the Cu sample, indicating that a rather large and unique process is taking place at this low temperature. In addition, a gradual recovery rate is observed for all metals in the temperature range 50°K to 220°K. Near 220°K more rapid annealing processes take over until

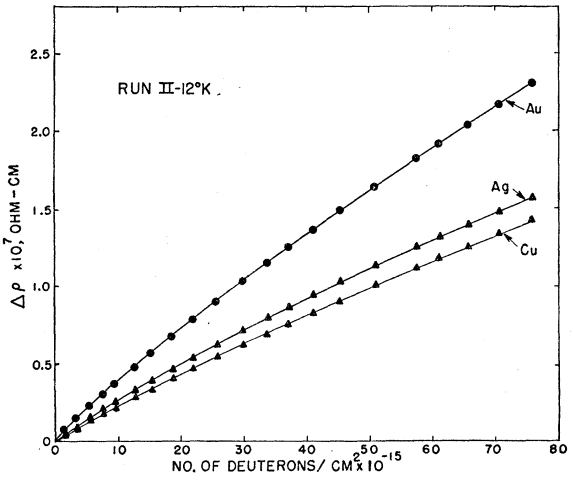

FIG. 5. Resistivity increase as a function of integrated deuteron flux—Run II.

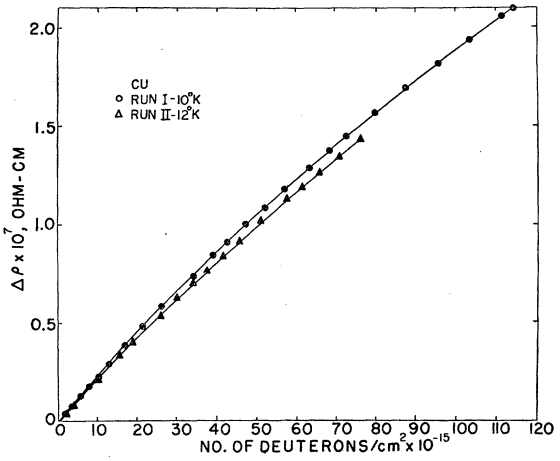

FIG. 6. Comparison of the resistivity increase produced in Cu during Run I and Run II.

[7] D. S. Billington and S. Siegel, Metal Progr. 58, 847 (1950).

temperatures of 250°K–280°K are reached, where recovery then proceeds at extremely slow rates.

In order to reduce the gas burst effects in Run II, the cryostat vacuum chamber was connected to the large cyclotron diffusion pumps and, as a result, the thermal pulse in the specimens persisted for less than a minute with a maximum temperature of about 30°K. The annealing curves observed in Run II are shown in Fig. 8. The percentages of $\Delta\rho_{max}$ that recovered during this pulse, shown by dashed lines near 15°K on the figure, were 5, 10, and 2 for Cu, Ag, and Au respectively, as compared to 28, 23, and 4 percent

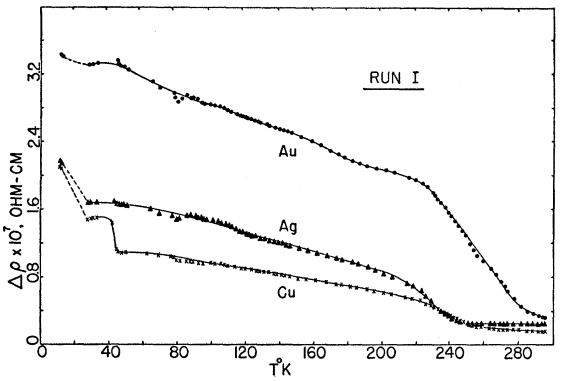

FIG. 7. Thermal recovery during warmup from 10°K to 300°K —Run I. The resistivity increase remaining at temperature T is plotted *versus* T.

respectively for the larger effect in Run I. In the temperature range 35°K–45°K on Fig. 8, 40 percent of $\Delta\rho_{max}$ annealed in Cu, which clearly indicates that the large recovery observed in Cu during the gas burst of Run I would have occurred near 40°K if a gradual warmup had been made. In addition the improved technique made it possible to resolve an analogous drop in Ag near 30°K, where 13 percent of $\Delta\rho_{max}$ recovered between 27°K and 33°K. From the difference in the results on Cu between Run I and Run II, it appears that the ten percent of $\Delta\rho_{max}$ which disappeared in Ag during the thermal pulse would normally recover near 30°K also. No similar abrupt low temperature drop was observed in Au, and since all three metals have f.c.c. lattice structure, this seems rather surprising. Possible explanations are that this annealing process occurs below 10°K in Au or that the drop is too small to be resolved in this type of measurement. Because of the radiation shield at liquid nitrogen temperature, which surrounded the target block, the warmup rate became very slow in the temperature range 75°K–85°K during both runs and caused the anomalous dips in the annealing curves. The relative amounts of $\Delta\rho$ that remain at various annealing temperatures are tabulated for the two runs in Table II.

V. DISCUSSION

The theory of Seitz[1] predicts that the fractional concentration of interstitial atom and vacancy pairs, here-

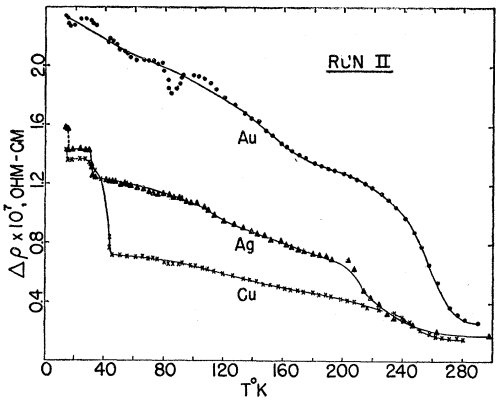

FIG. 8. Thermal recovery during warmup from 10°K to 300°K —Run II. The resistivity increase remaining at temperature T is plotted *versus* T.

after called I-V pairs, produced by an irradiation of 10^{17} deuterons/cm² is the order of 10^{-3} in Cu, Ag, and Au. When similar quantities of impurity atoms are added, *e.g.*, Ni in Cu, the resistivity increase is linear with the impurity concentration;[8] hence it seems reasonable that the same linear dependence should hold for the small quantities of defects which were induced in this experiment. The deviation from linearity observed in all of the $\Delta\rho$ *vs* n curves, shown in Figs. 4 and 5, should then be direct evidence that annealing of some nature does occur at irradiation temperatures as low as 10°K. It has previously[2] been pointed out that if there is no recovery during the bombardment other than radiation annealing, then the differential production of lattice defects could be described by the relation

$$dN=\alpha dn-\beta N dn, \qquad (1)$$

where N is the number of I-V pairs per unit volume, n is the number of incident particles per unit area, α is the number of I-V pairs produced per particle in a unit distance, and β is the probability that one existing pair per unit volume would be annihilated through the action of one fast particle per unit area. The integration of this equation and the assumption that $\Delta\rho$ is proportional to N result in the following theoretical ex-

TABLE I. Summary of bombardment data obtained near 10°K.

Run	Sample	$10^{-17}\times$flux d/cm^2	$10^{7}\times\Delta\rho_{max}$ Ω-cm	$\Delta\rho_{max}/\rho_0$ [a]
I	Cu	1.1	2.1	0.13
I	Ag	1.1	2.2	0.15
I	Au	1.1	3.4	0.15
II	Cu	0.8	1.4	0.09
II	Ag	0.8	1.6	0.11
II	Au	0.8	2.3	0.10

[a] ρ_0 = resistivity at 0°C.

[8] D. K. C. MacDonald and W. B. Pearson, Phys. Rev. 88, 149 (1952).

TABLE II. Fraction of the initial resistivity increase that remains at various annealing temperatures.

Run	Sample	$\Delta\rho/\Delta\rho_{max}$ remaining at 35°K[a]	45°K	77°K	220°K	300°K
I	Cu	···	0.53	0.48	0.26	0.07
I	Ag	···	0.76	0.70	0.31	0.10
I	Au	···	0.97	0.87	0.57	0.10
II	Cu	0.89	0.49	0.41	0.25	0.08
II	Ag	0.77	0.76	0.69	0.27	0.10
II	Au	0.98	0.93	0.86	0.51	0.10

[a] Annealing data at 35°K for Run I was invalidated by a gas burst.

pression for the bombardment curves:

$$\Delta\rho = A(1-e^{-\beta n}). \quad (2)$$

This equation predicts a saturation value of $\Delta\rho_s = A$ for large fluxes, when the rate of radiation annealing becomes equal to the rate of I-V pair production.

It was found that Eq. (2) would not satisfactorily describe the $\Delta\rho$ *vs* n curves obtained for Cu, Ag, and Au near liquid nitrogen temperature;[2] and it then appeared that this discrepancy was due to the accumulation of secondary defects, possibly in the form of defect clusters. However, when this expression was fitted to the irradiation data of the present investigation, close agreement was achieved for all metals. The fact that the nonlinearity in all of the curves can be accounted for by Eq. (2) forms rather strong evidence that the primary source of recovery during the liquid helium bombardments is radiation annealing. The values of A, β, the maximum deviation from the measured points, and the initial slopes for the best theoretical curves are given in Table III. This information serves as a more accurate definition of the data plotted in Figs. 4 and 5. It is interesting to note that the annihilation probability of I-V pairs, β, is about the same for all three metals, which tends to confirm that the internal structure of Cu, Ag, and Au is quite similar. The Ag specimens had the highest β value; this indicates that more thermal recovery may have occurred for this metal, since there is a sizeable annealing process near 30°K, as shown in Fig. 8.

As mentioned above, the similar electronic structure of Cu, Ag, and Au should allow at least qualitative conclusions to be made from the $\Delta\rho$ data in regard to the Z-dependence of the irradiation effects. It is seen from Fig. 4 that, for the bombardments made near liquid nitrogen temperature, the $\Delta\rho$ values are larger as the atomic number Z increases; and that this same relation still exists for the data obtained near 10°K. The theoretical Z-dependence, calculated by Seitz,[1] is given to a good approximation by the relation

$$(dE/dx)_{c,d} \propto Z^2 N_0/M, \quad (3)$$

where $(dE/dx)_{c,d}$ is the rate at which deuteron energy is lost to those collisions which result in I-V pair displacements, N_0 is the number of metal atoms per unit volume, and M is their atomic mass. The minimum energy required for the production of an I-V pair is expected to be about the same for all three metals;[1] thus the proportionality factor between $(dE/dx)_{c,d}$ and defect concentration should be nearly equal for Cu, Ag, and Au, and would cancel out when ratios relative to Cu are taken. The initial slopes of the $\Delta\rho$ *versus* n curves presumably would represent the results for the ideal case where all of the induced I-V pairs are retained in the metal, i.e., no radiation or thermal annealing, and hence this particular irradiation data should be the best for use in a check with theory. Table IV contains a comparison, relative to Cu, between the theoretical and observed Z-dependence of the irradiation effects. The theoretical ratios are calculated from Eq. (3) and the experimental ones are obtained from the initial slopes of the $\Delta\rho$ *vs* n curves, that are tabulated in the last column of Table III. The rather good agreement with theory, in view of the approximations involved, indicates that the Z-dependence calculated by Seitz is quite accurate.

TABLE III. Results from fitting Eq. (2) to the experimental irradiation data.

Run	Sample	A $\mu\Omega$-cm	$10^{17}\times\beta$ cm$^2/d$	Maximum deviation in percent of $\Delta\rho_{max}$	Initial slope[a] $(=A\beta)$
I	Cu	0.519	0.450	0.3	0.234
I	Ag	0.396	0.690	0.6	0.273
I	Au	0.749	0.530	0.7	0.397
II	Cu	0.513	0.430	0.3	0.221
II	Ag	0.398	0.660	0.4	0.263
II	Au	0.612	0.620	0.6	0.379

[a] Initial slope is given in units of $\mu\Omega$-cm per 10^{17} d/cm^2.

TABLE IV. Z-dependence comparison of irradiation effects in Ag and Au relative to Cu.

	Ratio of observed initial $\Delta\rho$ *versus* n slopes Run I	Run II	Theoretical ratio from Eq. (3)
Ag/Cu	1.16	1.19	1.07
Au/Cu	1.70	1.71	1.67

The determination of the absolute I-V pair concentrations from the $\Delta\rho$ data is complicated by uncertainties in the contribution of a single pair to the conduction electron scattering. Jongenburger[9] has calculated that one percent of vacancies in Cu, Ag, and Au would increase their resistivity by 1.3, 1.5, and 1.5 μohm-cm respectively. Unfortunately, similar work has not been carried out for interstitial atoms; however, if it is assumed that the interstitial and vacancy make equal contributions to $\Delta\rho$, his calculations in conjunction with the initial $\Delta\rho$ *versus* n slope data from Table III yield the results that 10^{17} deuterons/cm^2 would produce 0.09, 0.09, and 0.13 percent of I-V pairs in

[9] P. Jongenburger, Appl. Sci. Research **B3**, 237 (1953).

Cu, Ag, and Au respectively. The corresponding values obtained from the Seitz theory are 0.2, 0.3, and 0.6 percent. Overhauser[10] has made calorimetric measurements on the energy released when I-V pairs recombine in Cu. He observes that an energy of 1.7 cal/g is liberated when 1 μohm-cm of resistivity is recovered. If it is assumed that the energy from a single pair is 5 ev, then one may conclude from his data that one percent of I-V pairs in Cu would increase ρ by 11 μohm-cm; this would imply, from Jongenburger's value for vacancies, that the interstitital contribution to $\Delta\rho$ is about seven times greater than that from vacancies. When the 11 μohm-cm factor is applied to the initial slope data, one finds that the amount of I-V pairs created by 10^{17} deuterons/cm^2 is 0.02 percent in Cu, which is about one-tenth of the theoretical value. It seems highly unlikely that the interstitial electron scattering is more than a factor of ten greater than that from a vacancy; so it should be safe to conclude that, on the basis of Jongenburger's calculations, agreement between experiment and theory for the absolute magnitude of the defect concentrations induced in Cu, Ag, and Au is obtained to within an order of magnitude.

An estimate of the total number of metal atoms, denoted as Q, that are heated above the annealing temperature when one I-V pair is produced may be made if the values of α and β are known. Since α is the total number of pairs produced in a unit distance by one deuteron and β is the annihilation probability for one I-V pair per unit volume per incident deuteron, Q is given by the quantity $\beta N_0/\alpha$, where N_0 is the number of metal atoms per unit volume. Now if K is denoted as the resistivity increase due to one I-V pair per unit volume, then α may be expressed by the equation $\alpha=A\beta/K$, where A is defined in Eq. (2). Upon assuming that one percent of I-V pairs in Cu increases the resistivity by 2.6 μohm-cm, one obtains from the values of A and β in Table III that $\alpha=740$ I-V pairs/cm for each 12-Mev deuteron incident on Cu. From this value for α and the relation given above for Q, one may then conclude that Q is 500 atoms per I-V pair created in Cu. If the shape of the "anneal zone" is taken as spherical, the radius associated with the above Q value is less than four lattice parameters. Corresponding figures for Ag and Au may be obtained and will be similar to those of Cu, providing that comparable values for K are assumed.

The general behavior of the annealing phenomena, occurring during the warmups from 10°K to room temperature, may be grouped into three temperature ranges: 1. Low, below 50°K; 2. Intermediate, 50°K–220°K; and 3. High, 220°K–280°K. Previous[2–4] isothermal studies on Cu, Ag, and Au have been made in the intermediate and high regions, with most of this work confined to Cu. A wide spread of activation energies for migration, which were substantially proportional to the absolute temperature of the isothermal anneal, were found for the processes recovering in the intermediate region in Cu; while only a single activation energy, of 0.68 ev for Cu, was observed in the high range. It appears[3] that the process in the latter case is of second order, i.e., $dN/dt \propto N^2$, and may therefore be ascribed to the volume diffusion of either interstitial atoms or vacancies. At the present time, there does not seem to be sufficient evidence for an unambiguous choice between the two possibilities. Although this high temperature recovery has not previously been studied in detail for Ag and Au, the annealing curves of Figs. 7 and 8 indicate that the process occurs at about the same temperature for all three metals and presumably it is due to the same mechanism in all cases. However, as seen from Table II, a considerably larger percentage of $\Delta\rho_{\max}$ is recovered in Au than in Cu or Ag during the anneal from 220°K–280°K; it is very probable that this difference is related to the apparent absence of a low temperature process in Au.

Recently T. H. Blewitt (as yet unpublished work) has discovered that no recovery occurs in the intermediate range for neutron irradiated Cu single crystals, where the total induced I-V concentration is small and about equivalent to that from 10^{15} deuterons/cm^2. A possible reason for this result is the absence of grain boundaries; another is the relatively dilute amount of I-V pairs, since the $\Delta\rho$ *versus* n curves for the present experiment were essentially linear up to a flux of 10^{16} deuterons/cm^2. It has previously[2,3] been suggested that the intermediate annealing may be due to pairs in which the interstitial and vacancy are very close to each other and the energy barrier between them is lowered by the interactions. A spectrum of activation energies could then be obtained from the various spacings that exist within the region of appreciable mutual influence; however, Seitz[11] has pointed out that the frequency factors observed for these processes are several orders of magnitude below the expected value of around 10^{12} sec^{-1}. In view of this fact it now appears that some other mechanism, *e.g.*, defect clusters such as divacancies; or defect traps in the form of impurity atoms, grain boundaries, or dislocations, is responsible for the intermediate processes.

The present experiment reveals that in addition to these previously observed recoveries, a very unique process takes place in both Cu and Ag below 50°K which is denoted as the low temperature process in this discussion. During Run II, these phenomena were manifest through the disappearance of 40 and 13 percent of $\Delta\rho_{\max}$, for Cu and Ag respectively, in corresponding temperature intervals of 35°K–45°K and 27°K–33°K. Under ideal experimental conditions it is estimated that the above values would be about 50 percent for Cu and 25 percent for Ag; it is also possible that a somewhat smaller effect, certainly less than 10 percent of $\Delta\rho_{\max}$, may be resolved in Au if very precise

[10] A. W. Overhauser, Phys. Rev. **94**, 1551 (1954).

[11] F. Seitz (private communication).

annealing techniques are used. The time rate of the low temperature recovery in Cu was maximum at 43°K and, if an extrapolation is performed on activation energy data obtained by Overhauser[3] in the range 90°K–270°K, this recovery temperature would correspond to a process with an activation energy for motion of 0.1 ev. The analogous maximum occurred at 30°K in Ag and, since the activation energies observed in Cu and Ag at −165°C are the same,[2] it is expected that the low temperature activation energy for Ag is near 0.1 ev also.

Huntington[12] has recently calculated the energy for migration of interstitial Cu atoms in Cu and obtained results of 0.07 and 0.24 ev, for the two types of interaction potentials that were considered. Previous theoretical computations[13,14] of the activation energy for the motion of vacancies in Cu yielded values of around 1 ev. These theoretical results would then indicate that the low temperature (0.1 ev) process in Cu should be assigned to interstitial motion and the high temperature (0.68 ev) process to vacancy motion. These assignments would imply that both the 0.1 and 0.68 ev processes be approximately second order; I-V pair annihilation would result precisely in a bimolecular reaction, however, if some of the migrating defects are trapped slight deviations from second order may be expected. This has been observed for the 0.68 ev process, but it appears that additional work such as the formidable task of isothermal annealing at 40°K is necessary for definite establishment of the low temperature kinetics. The question of how vacancies can be annihilated in a second order fashion, when they begin to diffuse rapidly, arises. This could be accomplished by the coagulation of two vacancies into a divacancy, for Bartlett and Dienes[15] have calculated that the activation energy for migration of the latter is lower than that of vacancies; hence the divacancies could move to traps, such as dislocations or the surface, within a very short time and their formation should then be equivalent to vacancy annihilation. In addition, the presence of interstitial traps or clusters, which have activation energies for motion of 1 ev or more, could account for this phenomena, although it is questionable at the present time whether such aggregations do exist.

It is also possible that the low temperature process may be due to close I-V pairs. This was previously discounted as the source of intermediate recovery, because of discrepancies in the frequency factor; however, if the interactions between the interstitial and vacancy are very short range, there is the potentiality that only stable I-V pairs with the very smallest separations have their activation energies altered and hence their annihilation would result in a unique process. A sizable fraction of the defects could possess this configuration since many of the secondary and tertiary knock-on atoms do not have appreciable energy above that of the displacement threshold.[1] Such correlated pairs would result in a first order process and hence a determination of the kinetics should decide between the possibilities of close pairs and a second order recovery, such as interstitial motion, for the low-temperature process.

From Table II it is seen that about ten percent of the initial resistivity increase still remains in all metals at 300°K. Recent studies of recoveries in electrical resistivity[4] and critical resolved shear stress,[16] made in the region above room temperature, reveal that an annealing process with an activation energy of about 2 ev, which is nearly the same value as that observed for self-diffusion in Cu, proceeds at an appreciable rate near 300°C in irradiated Cu. The source of this process is likely to be associated with dislocations, since a relatively large proportion of the radiation-induced resolved shear stress increase anneals in this very high temperature range.

VI. SUMMARY

1. Near 10°K the initial rate of resistivity increase with the integrated deuteron flux is 0.23, 0.27, and 0.36 μohm-cm per 10^{17} deuterons/cm^2 respectively for Cu, Ag, and Au.

2. The Z-dependence of the resistivity increase induced in Cu, Ag, and Au by the radiation varies essentially as Z^2N_0/M, as predicted by the theory of Seitz.

3. No thermal recovery occurs when the deuteron beam is turned off and the specimens are held near the bombarding temperature.

4. The $\Delta\rho$ *versus* n curves deviate from linearity at high deuteron fluxes and this "bending over" may be accounted for by radiation annealing.

5. A very rapid low temperature recovery is observed in Cu near 43°K and in Ag near 30°K. Between 40 and 50 percent of the initial resistivity increase in Cu and from 13 to 24 percent of the initial increase in Ag anneals within a temperature interval of ten degrees absolute for these processes.

6. In the temperature range 50°K–220°K, a gradual recovery occurs for all three metals during which about 24, 47, and 41 percent of $\Delta\rho_{\max}$ disappear in Cu, Ag, and Au, respectively.

7. Near 220°K the recovery rate becomes more rapid in all metals, which persists until temperatures of 250°–280°K are reached, where it then proceeds at an extremely slow rate. It was previously established that a second order process took place in this region for Cu and this investigation indicates that it also occurs in Ag and Au at nearly the same temperature. This process accounts for 18, 19, and 44 percent of $\Delta\rho_{\max}$ in Cu, Ag, and Au, respectively.

8. The percentages of the initial resistivity increase

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[13] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).
[14] H. B. Huntington, Phys. Rev. **61**, 325 (1942).
[15] J. H. Bartlett and G. J. Dienes, Phys. Rev. **89**, 848 (1953).
[16] Redman, Coltman, and Blewitt, Phys. Rev. **91**, 448 (1953).

remaining at 300°K are 8, 10, and 10 for Cu, Ag, and Au, respectively.

VII. ACKNOWLEDGMENT

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Measurements of Electrical Conductivity and Magnetoresistance of Gray Tin Filaments*

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A method for the preparation of gray tin filaments suitable for electrical measurements is described. Results of measurements of the temperature dependence of the electrical conductivity and of the magnetoresistance on pure gray tin and on alloys containing various amounts of Sb, As, In, Al, and Zn are reported. For 99.998 percent pure tin the activation energy is 0.082 ev and the conductivity at 0°C is 2090 ohm^{-1} cm^{-1}. Addition of impurities results in an increase in the "intrinsic" activation energy and a decrease in the absolute value of the conductivity in the "intrinsic" range. Samples doped with *n*-type impurities exhibit a positive temperature coefficient of resistance at low temperatures whereas the low-temperature conductivity of *p*-type samples becomes temperature-independent at high impurity concentrations. The three *p*-type impurities In, Zn, and Al show marked differences in their effectiveness in producing *p*-type conductivity, In being 40 times more effective than Al. The magnetoresistance coefficient in the lattice-scattering region shows a stronger temperature dependence than is predicted by the simple theory. Impurity scattering appears to be relatively more important in *p*-type than in *n*-type material.

I. INTRODUCTION

IN 1950 Busch, Wieland, and Zoller[1] found that gray tin is a semiconductor similar to the other Group IV elements, carbon (in the form of diamond), silicon, and germanium. The subsequent investigations by Busch and his collaborators[2–4] and by Kendall[5,6] have revealed many of the semiconducting properties of gray tin. The measured values of some of the most important quantities have remained uncertain, however, because of the difficulty of preparing suitable specimens. The only method of obtaining gray tin is through the well known phase transition from the metallic phase. More direct methods, such as evaporation onto a cold substrate or electrolytic deposition at reduced temperatures, though tried by several investigators, have not proved successful. Using the phase transition method one generally obtains gray tin as a powder because of the large volume expansion associated with the white-to-gray transformation. Using such powder samples, Busch and his co-workers have measured the Hall coefficient, the magnetoresistance coefficient, the temperature dependence of the conductivity and the magnetic susceptibility. They conclude however that neither high-frequency loss measurements nor direct conductivity measurements made on powder are suited to an exact determination of the absolute value of the conductivity. Kendall has used two types of samples, lumps selected from a large quantity of powder and rods of compressed powder. Only an approximate value of the conductivity could be determined using the first type because of the difficulty in measuring the cross section and electrode areas. While this difficulty was eliminated through the use of compressed-powder rods, measurements on these samples yielded an unusually low value of the activation energy and therefore the value of the specific conductivity obtained using them is also open to question. In view of these difficulties, need for an improved method of preparing gray tin samples has been recognized. More suitable specimens were needed both to establish precise and reliable values of previously measured quantities, especially the value of the specific conductivity, and to extend the investigation to include phenomena such as the thermoelectric effect and photoelectric effect.

In searching for an improved method of preparation one of us[7a] found that fine wires of metallic tin would transform to the gray phase without the usual crumbling

* Parts of this material were reported at the North Carolina and Michigan meetings of the American Physical Society [Phys. Rev. 91, 244 (1953); Phys. Rev. 94, 1428 (1954)].

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