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Isothermal Annealing Effects in Irradiated Copper*

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Copper wires were bombarded with 12-Mev deuterons at low temperatures. The wires were then allowed to anneal isothermally at successive temperatures from −185°C to +167°C. Recovery of the electrical resistivity increase, produced by the bombardment, was observed at all temperatures. The annealing curves obtained for temperatures between −185°C and −60°C were of such a character that only a number of processes with different activation energies could account for them. One-half of the resistivity increase recovered in this range. The activation energies obtained were observed to be proportional to the absolute temperature. A value of 0.44 ev was found near −100°C. Above −60°C the annealing behaved as though it were a single process with a unique activation energy. This process accounted for 25 percent of the increased resistivity and had an energy of 0.68 ev. At room temperature 25 percent of the increase remained, and further anneals to temperatures as high as 167°C produced only an additional 4 percent recovery.

Detailed analysis of the data suggests that the single process occurring above −60°C is the result of the annihilation of interstitial atoms and vacancies that are produced by the irradiation. Slight deviations of the recovery rate from that expected of such a second-order process were observed and could be explained as the effect of elastic strains introduced into the lattice by interstitial atoms. The effect of such lattice strains on the rate of vacancy migration was calculated and found to have sufficient magnitude to explain the data. The results also suggested that the low temperature recovery is due to the correlated annihilation of very close interstitial vacancy pairs, the low activation energies being due to large elastic strains in the immediate vicinity of an interstitial. A further result, which can be derived from the activation energy for self-diffusion in copper, is that the energy of formation of a vacancy is 1.39 ev.

I. INTRODUCTION

THE experiments described here were undertaken as part of the general program of the radiation damage group at Illinois in studying the basic properties of the lattice imperfections introduced into metals by bombardment with fast particles. Many of the physical properties of a metal are altered by the presence of such imperfections, but changes in electrical resistivity are perhaps the easiest to study experimentally. Previous work[1] has shown the amount of resistivity changes resulting from irradiation and the fact that most of these changes anneal out at low temperatures. The types and quantities of lattice defects needed to account for the observed changes cannot be settled without more detailed investigations, both experimental and theoretical. Interstitial atoms and vacancies are certainly among the defects produced during bombardment,[2] but the effect of such defects upon the electrical resistance of a metal is not known accurately.

The present annealing studies were planned with the hope that they might shed some light on these general questions. Copper was chosen for bombardment because it has been the subject of much theoretical study and was most suited to the special experimental techniques employed. The specimens were bombarded by 12-Mev deuterons in the Illinois cyclotron and were then transferred to the laboratory for subsequent anneals in various constant temperature baths. The changes in electrical resistance with time were measured during each step of the thermal treatment.

II. DESIGN OF SAMPLES

The increase in electrical resistivity resulting from a bombardment of 10^{17} deuterons/cm^2 is about $7\cdot10^{-8}$ ohm-cm. At any one temperature, only a fraction of this increase will anneal out, so that it is desirable to have a sensitivity of 10^{-11} ohm-cm. Temperature fluctuations of 0.1°C will cause variations in resistivity of about 10^{-9} ohm-cm. If ordinary potentiometric techniques are used for such measurements, it is clear that such temperature fluctuations will mask the small effects that are of interest.

* This research was supported by the U. S. Atomic Energy Commission.
[1] Marx, Cooper, and Henderson, Phys. Rev. 88, 106 (1952).
[2] F. Seitz, Disc. Faraday Soc. 5, 271 (1949).

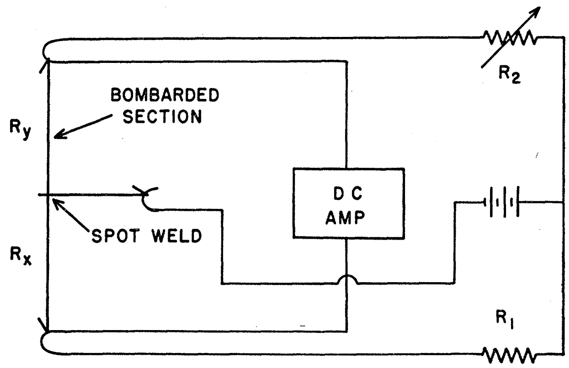

FIG. 1. Schematic diagram of a bombarded specimen and the bridge circuit used in the resistance measurements.

A bridge method was employed in order to eliminate the effects of temperature variations. The bridge was constructed by spot welding a 10-mil copper lead to a 5-mil copper wire. Both ends of the 5-mil wire were then bent over sharply at a distance of one inch from the spot weld. The two halves of the 5-mil wire then formed two arms, R_x and R_y, of the bridge circuit shown in Fig. 1. The lead wires shown in the figure were soldered to the specimen after the section R_y had been bombarded in the cyclotron. The solder connections were made while the sample remained in liquid nitrogen by letting only the ends protrude above the surface. The bombarded section of R_y was $\frac{1}{2}$ inch in length and did not warm up during the soldering operation. The lengths of the two arms, R_x and R_y, were equal to better than 1 percent in all cases. Therefore, temperature fluctuations caused almost equal variations in the resistance of the two arms, so that the balance of the bridge was not affected.

The other two arms of the bridge consisted of identical decade boxes. R_1 was fixed at 450 ohms whereas R_2 was varied in 0.1-ohm steps. A Perkin-Elmer dc breaker amplifier was used as the detection device because of its high sensitivity and speed. The output of the amplifier was filtered and fed into a standard zero center millivoltmeter, which was used to interpolate between the settings of R_2. Each arm of the bridge carried 0.04 amp, so that a resistivity change of 10^{-11} ohm-cm in the bombarded wire produced a signal of 4×10^{-9} volt, which was detectable. Stray emf's were eliminated by zeroing the amplifier with the bridge current off.

III. TEMPERATURE BATHS

The constant temperature baths were controlled with a standard bimetal thermoregulator. Between $-125°C$ and $-70°C$ the baths were of pentane and were cooled by a glass tube filled with liquid nitrogen. Between $-70°C$ and room temperature the baths were of acetone and were cooled with a tube of dry ice. Light paraffin oil was used for baths above room temperature.

Temperatures were measured with a calibrated five-junction copper constantan thermopile. The temperature fluctuations of all the baths were several hundredths of a degree about the mean.

IV. TRANSFER OF SAMPLES

During bombardment, the samples were fixed to a target block, supported by a flask of liquid nitrogen. The samples were pressed against the target block at their upper ends by spring arms from a rotating shaft. Torque was applied to this shaft by a length of fuse wire. A small Dewar flask was placed inside the vacuum cryostat just below the samples. After bombardment this small Dewar was filled with liquid nitrogen from a transfer system entering through the bottom of the cryostat. The fuse wire was then blown out and the samples fell into the liquid nitrogen. They were then removed from the cyclotron and stored in liquid nitrogen until the annealing studies were made. A small light was mounted inside the cryostat, and the entire transfer operation could be observed through an optical port.

A thermocouple was attached to one of the samples that was mounted in the foregoing way so that the temperature history of the samples could be recorded. The thermal junction was made at the lowest point of the sample which was still in the deuteron beam. The temperature of this point was $-165°C$ with the beam off and $-145°C$ with the beam on. When liquid nitrogen was admitted into the Dewar flask, the temperature rose to $-100°C$ for several seconds and then dropped to $-130°C$ for about one minute, at which time the samples were dropped. The effect of this short thermal pulse was found to be unimportant. It was necessary, however, to precool the transfer system in order to prevent a large thermal pulse at the beginning of the transfer. The cryostat had to be opened to air at this time in order to permit the flow of liquid nitrogen.

V. PROCEDURE

The copper wires to be bombarded, which were 99.99 percent in purity, were annealed in a high vacuum at 400°C for five hours. They were then attached to the target block as described in Sec. IV.

In addition to the wires to be dropped, one specimen was fixed permanently to the cooling block so that electrical measurements could be made during the irradiation. This wire was in contact with the cooling block at its lower end and insulated by a $\frac{1}{2}$-mil mica strip at its upper end. Copper constantan thermal junctions were spot welded near the upper and lower ends, and the copper leads of these junctions also served as potential leads for resistance measurements. The potentiometric techniques used on this sample were those described previously[1] with the current, the IR drop, and the two temperatures being measured simultaneously. The cooling of this specimen was quite efficient, since its temperature was about $-180°C$ with the beam on and six degrees colder with the beam off. After the main deuteron bombardment the increased resistance of this sample was observed to anneal appreciably at −185°C. A short rebombardment was then made in order to study the effects of thermal annealing on the bombardment data.

The deuteron flux was measured by a current integrator attached to the target block. The necessity of dropping the samples precluded the use of a Faraday cage so that absolute values of the flux had to be estimated by comparison with previous data.[1] An additional check was provided from the induced Zn^{65} activity in the copper specimens. After the bombardment was completed, the samples were transferred to the laboratory according to the procedure described in Sec. IV.

Connections to the bridge circuit were made as shown in Fig. 1 and described in Sec. II. Each sample was annealed at successively increasing temperatures. The time of anneal at any one temperature varied from one to three hours, and about 30 measurements of R_2 were made for each anneal. The resistance, R_x, of the undamaged half of the sample, which formed one arm of the bridge, was measured at every temperature by potentiometric methods. It was therefore possible to determine the absolute changes in resistance of the irradiated section. Let r be the resistance increase in the bombarded wire due to the radiation damage, and let t be the time. The variation in r with time at a fixed temperature is then given by

$$dr/dt = (R_x/R_1)dR_2/dt. \quad (1)$$

Since the resistance r is independent of temperature, as is shown below, it is possible to determine the value of r at every stage of the thermal treatment. Let R_x, R_y, and R_2 be the measured values at the last point of one temperature anneal and R_x', R_y', and R_2' be the values for the initial point of the next temperature anneal. Since the contribution of the natural resistance (thermal and impurity) to R_y is proportional to R_x, we have

$$(R_y - r)/R_x = (R_y' - r)/R_x'. \quad (2)$$

From (2) and the bridge balance conditions for both temperatures, we find

$$r = R_x R_x'(R_2 - R_2')/R_1(R_x' - R_x). \quad (3)$$

The changes in r for an anneal at one temperature as determined from (3) were consistent with the values obtained from the integral of (1).

The experimental agreement obtained between values from (1) and (3) for the total amount of recovery can be used to show that Matthiessen's rule is valid for the resistance due to radiation damage in the temperature range from −125°C to room temperature; that is, r is independent of the temperature, T. In order to demonstrate the importance of such agreement, let us assume that between −125°C and room temperature r has the temperature dependence

$$r = r_0(1 + aT).$$

Then, we would compare changes in r_0, so that (1) would be replaced by

$$dr_0/dt = R_x(dR_2/dt)/R_1(1 + aT). \quad (4)$$

Equation (3) would be replaced by

$$r_0 = R_x R_x'(R_2 - R_2')/R_1(R_x' - R_x)(1 + ab). \quad (5)$$

Here

$$b = (R_x'T - R_xT')/(R_x' - R_x).$$

The value of b was calculated and found to be about 45 for all temperatures, and T was about 220°K on the average. Thus, values for the recovery obtained from (4) would be divided by an extra factor $(1 + 220a)$, whereas values from (5) would be divided by a factor $(1 + 45a)$. The differences introduced by these extra factors would cause a discrepancy of 4 percent in the computed recoveries if a were as large as 0.0002. Such a disagreement would have been apparent, so that we can conclude that Matthiessen's rule obtains, or at least that a is less than 0.0002, and that (1) and (3) are sufficient for the analysis of the experiment.

Activation energies were calculated for each stage of the recovery process from the ratio, R, of the initial value of dr/dt at a given temperature and the final value of dr/dt for the preceding temperature. Since dr/dt is proportional to $\exp(-E/KT)$, we have:

$$E = KTT'(\log R)/(T' - T). \quad (6)$$

This method of determining activation energies has the advantage that it depends only upon the data from a single sample; that is, r is known to be the same for the two reaction rates involved.

VI. RESULTS

The increase in resistivity of copper as a function of deuteron flux is shown in Fig. 2 for the sample which was mounted permanently to the target block and which was cooled to −180°C during the bombardment.

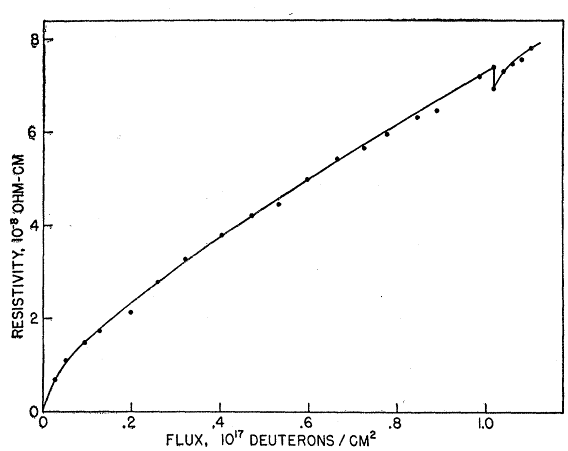

FIG. 2. Resistivity increase *versus* deuteron flux at a temperature of −180°C. The decrease at a flux of 10^{17} was due to thermal recovery.

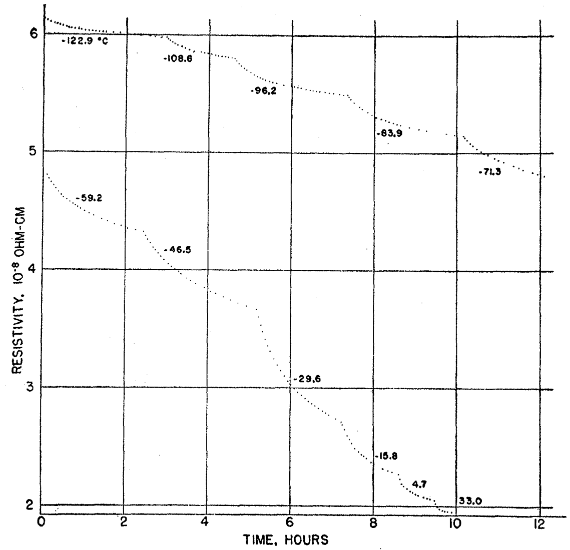

FIG. 3. Isothermal annealing curves from a single specimen at temperatures between $-123°C$ and room temperature.

The beam intensity was about 10^{15} deuterons/cm^2 per hour ($4\cdot 10^{-8}$ amp/cm^2) so that the bombardment lasted over five days. The bending of the curve at a flux around 0.1×10^{17} deuterons/cm^2 should be noted. The initial slope is larger by about a factor of 4 than the slope of the remainder of the curve.

At a flux of 1.0×10^{17} the bombardment was stopped and the temperature of the wire dropped to $-185°C$. Appreciable annealing was observed at this temperature, and 6 percent of the increase recovered after 22 hours. A short rebombardment was then made and the resistivity again increased rapidly at first and appeared to bend (Fig. 2) into the extension of the initial bombardment curve.

This behavior suggests that irradiation introduces lattice imperfections which anneal out at liquid nitrogen temperatures and below. Thus, when bombardment begins, the number of such imperfections increases to a steady-state value determined by the rate of bombardment and the rate of thermal recovery. Within experimental error, all of the initial bending appears to be due to such mechanisms. Annealing effects from the bombarding particles and their attendant thermal spikes need not be postulated to explain this bending. Although recovery effects due to thermal spike action probably occur, they do not appear important in copper at deuteron fluxes of 10^{17}. Experiments at liquid helium temperatures should be decisive with regard to these questions.

An activation energy was estimated for annealing processes around $-180°C$ from the rate of the $-185°C$ anneal and the rate of bending on bombardment. A value of 0.20 ev was obtained.

Typical recovery curves obtained for anneals in the constant temperature baths are shown in Fig. 3, which is the data from a single specimen. The feature that should be noted in the temperature region below $-60°C$ is that each successive increase in temperature produces about the same additional recovery. Such behavior indicates that there are several processes taking place, since the characteristic of a single thermally activated process is that recovery occurs in a relatively narrow temperature region, the rate being very small at lower temperatures and the process being exhausted at higher temperatures. Recovery in the temperature region near $-30°C$ appears to have this behavior.

A plot of the activation energies obtained from several samples by Eq. (6) is plotted in Fig. 4 as a function of the temperature at which each value was determined. This data gives further indication that below $-60°C$ recovery is due to several processes with differing activation energies. Those processes which have smaller energies cause recovery at lower temperatures, which is to be expected. The observed activation energy can represent, therefore, only an appropriate average value for the active processes at a given temperature, and may depend slightly upon the history of the sample. As is shown in Fig. 4, the energy observed at a given temperature is roughly proportional to the absolute temperature and is 0.44 ev at $-100°C$. On the other hand, the energy is constant in the vicinity of $-30°C$, so that this recovery appears again to be due to a single process. The activation energy obtained here is 0.68 ± 0.02 ev.

One specimen was annealed at $-18.3°C$ immediately after an anneal at $-90°C$, so that a complete recovery curve was obtained for the process that is active around $-30°C$. The experimental points for this anneal are shown in Fig. 5, and they are fitted with a curve which satisfies the equation

$$d(r-r_0)/dt=-A(r-r_0)^n. \qquad (7)$$

Here, r_0 is the resistivity increase due to irradiation that remains after this single annealing stage is com-

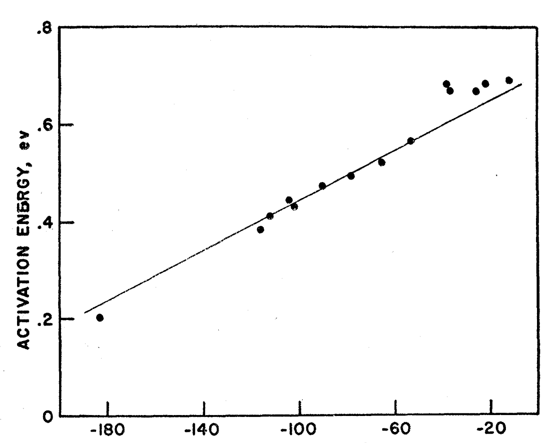

FIG. 4. Activation energy of the recovery process as a function of the temperature. The solid line is drawn through absolute zero.

pleted. Since the rate of recovery varied by a factor of 200 during the process, it was possible to determine accurately (to 0.1) the best value of n in (7). The best fit obtained was with $n=2.5$, and this curve is shown in the figure. This function, $(r-r_0)$, has the value $1.96\cdot 10^{-8}$ ohm-cm at $t=0$, which means that this unique recovery process accounts for 25 percent of the total resistivity resulting from radiation damage at -180°C.

In order to test further the hypothesis that annealing near -30°C is due to a single thermally activated process, a plot of the total recovery during the first 100 minutes at each successive temperature was made as a function of temperature from the data of one specimen. The points obtained are shown in Fig. 6, and the peak that would be characteristic of a single process is quite prominent. A calculation was then made for the values that such a single process would yield if it had suffered the same thermal treatment as the specimen. The constants used were those determined from the curve in Fig. 5 and the experimental activation energy of 0.68 ev. The solid lines in Fig. 6 connect the computed points and account entirely for the behavior in this temperature region.

The horizontal dashed line at the low temperature end of Fig. 6 indicates the average value at which similar points would have to be located in order to account for the observed recovery between -180°C and -100°C. The fact that the first two experimental points fall below this line is likely due to the short thermal pulse that occurred at the beginning of the transfer process from the cyclotron.

After room temperature anneals, 25 percent of the total resistivity increase remained. Further anneals to temperatures as high as 167°C produced only an additional 4 percent recovery. The soft solder connections weakened at higher temperatures.

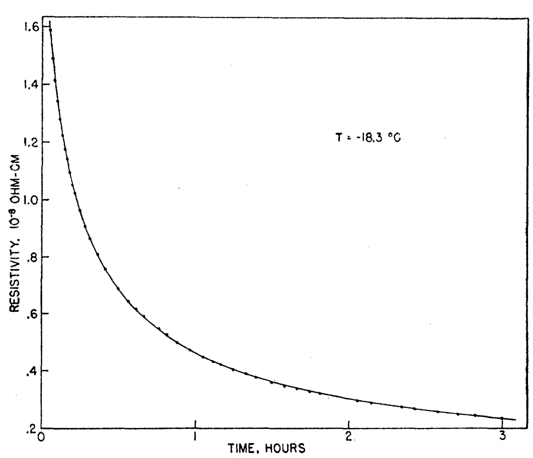

FIG. 5. Isothermal annealing curve for a specimen that was brought to -18.3°C after an anneal at -90°C. The solid curve is a solution of Eq. (7) of the text with $n=2.5$.

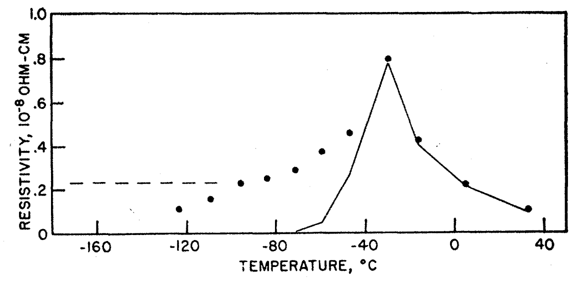

FIG. 6. Resistivity decrease during the first 100 minutes at each successive temperature for a single sample. The solid lines joint points that were computed for a single process with an activation of 0.68 ev.

VII. DISCUSSION

The shapes of the recovery curves above -40°C suggest that recombination of the interstitial atoms and vacancies, produced by the bombardment, occurs at these temperatures. Such annihilation will take place if either the interstitials or the vacancies, or both, begin to diffuse. Experiments on the quenching-in of lattice vacancies[3] in gold indicate that the vacancies begin to diffuse around -20°C. Experiments[4] on cold-worked copper and gold show that a stage of annealing in gold begins around -20°C, whereas the corresponding recovery in copper begins at about -40°C. These results suggest that the unique recovery process in irradiated copper is due at least to the migration of vacancies, and we shall assume for the purpose of discussion that the interstitial atoms are still stationary during this process.

Interstitial atoms and vacancies are produced in equal numbers by the bombardment. Let f be the atomic fraction of each. When the vacancies begin to migrate, we would expect the rate of annihilation to be governed according to a second-order process

$$df/dt=-cf^2. \quad (8)$$

Here, c would depend only upon the temperature. One might think that the possibility of vacancies colliding with each other to form divacancies would complicate matters. Theoretical estimates indicate that a divacancy would be stable, and also that the activation energy for motion of a divacancy would be about half the value for a single vacancy. A divacancy would then diffuse through the metal at a faster rate, by a factor of 10^6 or more, until it collides, perhaps, with an interstitial. The net result of the formation of a divacancy then, is the almost immediate annihilation of an interstitial, so that such processes can probably be neglected. The electrical resistance due to the interstitials and vacancies is proportional to f, so that we would expect the recovery to be described by (7) with $n=2$. We found however that $n=2.5$ provided a better fit in Fig. 5, and it also gave a better description of the observations in Fig. 6. We shall show that (8) should not apply,

[3] J. W. Kauffman and J. S. Koehler, Phys. Rev. **88**, 149 (1952).
[4] J. A. Manintveld, Nature **169**, 623 (1952).

except for very small concentrations, and that the correct expression is

$$df/dt = -cf^2e^{bf}. \qquad (9)$$

The extra exponential factor is due to the influence of elastic distortions produced by interstitial atoms on the migration of vacancies. The experimental curves are very well described by (9) if the value of bf is 0.8 at the beginning of the recovery process. The possibility that the extra steepness at the beginning of Fig. 5 may be due to the tail of the low temperature processes can be excluded, since the temperature of this anneal was sufficiently high that such processes (of lower activation energy) would have gone to completion in several minutes.

Vacancy migration results when adjacent atoms jump over the intervening potential barriers of height E, equal to the activation energy. The presence of other elastic strains will cause these potential barriers to be of different heights, and the net result is an increase in the average jump frequency. The elastic strains due to interstitial atoms in copper are about five times larger than those due to vacancies,[5] so that the latter can be neglected in comparison to the former, especially since the result depends upon the square of this magnitude.

The elastic displacement due to a spherical singularity in a homogeneous, isotropic, infinite medium is

$$\mathbf{u} = ga^3\mathbf{r}/r^3. \qquad (10)$$

Here, g is a dimensionless constant and we will let a be the lattice constant. The tensile strain along a line that makes an angle θ with the vector $\mathbf{r}$ is essentially the derivative of (10) and is given by

$$s = ga^3(1-3\cos^2\theta)/r^3.$$

Let us assume that there are N interstitial atoms per cc and that the volume is V, so that the total strain at a given point and in a given direction is

$$S = \sum_{i=1}^{NV} s_i. \qquad (11)$$

Since the divergence of (10) is zero, the compressive strain throughout the material is zero and the contributions to (11) will be positive as often as negative. Therefore, the probability distribution in S will be symmetric about $S=0$, and we shall estimate the second moment of the distribution. We have:

$$S^2 = \sum_{i,j} s_is_j.$$

The terms with $i \neq j$ will average to zero, and we obtain:

$$(S^2)_{\text{Av}} = (4/5)g^2a^6NV(1/r^6)_{\text{Av}}.$$

In order to estimate the average of $1/r^6$ we must introduce a cutoff at some distance r_0, of the order of magnitude of the lattice constant, which can be interpreted as the minimum distance of approach of an interstitial and vacancy such that annihilation does not necessarily result. Then

$$(1/r^6)_{\text{Av}} = 4\pi/3Vr_0^3.$$

We shall represent the distribution in S by a Gaussian function with the above second moment.

$$P(S) = (\beta/\pi)^{\frac{1}{2}}\exp(-\beta S^2). \qquad (12)$$

The coefficient β is:

$$\beta = 15r_0^3/128\pi g^2a^3f. \qquad (13)$$

We have replaced N by $4f/a^3$. We will need to know the joint probability function for the tensile strains S_x and S_y in two perpendicular directions at a given point. This distribution function $P(S_x, S_y)$ will not be the product of two factors corresponding to (12) since the strains are not independent; they are related by the condition that the compressive strain in zero. One can show that the required function is

$$P(S_x, S_y) = (2\beta/\pi\sqrt{3}) \times\exp[-\beta(S_x+S_y)^2-(\beta/3)(S_x-S_y)^2]. \qquad (14)$$

We must now estimate the change in barrier height caused by the presence of the elastic strains. This variation in the height of the saddle point over which the atoms must jump will be due mostly to changes in the ion-ion repulsive interaction which, in copper,[5] can be represented by a potential of the Born and Mayer type:

$$U = De^{-r/R}. \qquad (15)$$

If the migrating atom must jump between two atoms which are separated by a distance L, then the change in height of the saddle point due to a strain S along L is

$$\Delta E = -kS.$$

The constant k is determined from (15) and is

$$k = (DL/R)e^{-L/2R}. \qquad (16)$$

In copper the atom must jump between four atoms at the corners of a rectangle. The angle between the diagonals of this rectangle is $\alpha = 2\tan^{-1}(1/\sqrt{2})$, and the length of the diagonals is $L = (\frac{3}{2})^{\frac{1}{2}}a$. If we let the x and y axes lie in the plane of this rectangle so that they bisect the angles between the diagonals, then the change in barrier height due to elastic strains is

$$\Delta E = -2kS_x\cos^2(\alpha/2) - 2kS_y\sin^2(\alpha/2). \qquad (17)$$

The probability of jumping over the barrier will then be altered by the factor:

$$F = e^{-\Delta E/KT}.$$

We must average this factor over the distribution in elastic strain.

$$\bar{F} = \int P(S_x, S_y)e^{-\Delta E/KT}dS_xdS_y.$$

[5] G. J. Dienes, Phys. Rev. **86**, 228 (1952).

Evaluation of the above integral using (14) and (17) gives

$$\bar{F}=\exp[+k^2(1+3\cos^2\alpha)/4\beta K^2T^2].$$

We have shown, therefore, the presence of the exponential factor in (9), and from (13) the coefficient is

$$b=(128\pi/45)(gk/KT)^2(a/r_0)^3. \quad (18)$$

This value for b is not completely correct because the medium is not infinite as was assumed in describing the elastic strains by (10). One can show that a random distribution of singularities of concentration f in a bounded medium requires a pressure on the boundary if the elastic displacements are to be described by (10). The correct description of the elastic strain, then, is given by the previous solution, (11), plus a uniform volume expansion corresponding to a relaxation of the surface pressure. One can show that a uniform volume dilatation results of amount[6]

$$\Delta V/V=16\pi\gamma gf. \quad (19)$$

Here, γ is given by

$$\gamma=2(1-2\mu)/(1+\mu),$$

where μ is Poisson's ratio. The additional linear elastic strain is one-third the value of (19), so that the barrier heights are lowered by $(32\pi/3)\gamma gkf$. The complete expression for the coefficient b in (9) is then

$$b=(128\pi/45)(gk/KT)^2(a/r_0)^3+(32\pi\gamma/3)(gk/KT)(1-3\lambda), \quad (20)$$

where $\lambda=\exp[-(2-\sqrt{3})a/2\sqrt{2}R]$ and accounts for the lowering of the barrier minimum due to the same dilatation.

In order to test whether (20) is of the correct magnitude to explain the observations, we must know the concentration f_0 of interstitial atoms involved in the single annealing process. Estimates of the resistivity due to vacancies vary from[7] 0.4×10^{-6} ohm-cm to[8] 4.3×10^{-6} ohm-cm per atomic percent. If we assume that interstitials have the same resistivity, then f_0 would be between 0.23×10^{-4} and 2.5×10^{-4}. For copper, $a=3.6$A; D and R are determined from the elastic constants[9] and are 5.64×10^4 Rydbergs and 0.284 Bohr unit, respectively. The relaxation of atoms around an interstitial has been estimated[5] and gives a value for g of 0.06 if the calculated displacement of the cube corners is used in (10). If we let $r_0/a=1$, then (20) gives a value for b of 6×10^3, which is of the correct magnitude since bf_0 was observed to be 0.8. The second term in (20) is unimportant for this case since gk/KT is about 25.

The preceding theory is necessarily approximate, but it indicates that lattice strains resulting from an interstitial concentration of 0.01 percent can increase the rate of vacancy migration to a noticeable degree. Recent experiments[10] have shown that 1 percent of lead impurity enhances the self-diffusion in silver by a factor of 2. It appears that this effect can also be explained by the foregoing theory. The fact that the concentration of impurity atoms must be 100 times that of interstitials to produce comparable effects is due to the smaller relaxation of the neighboring atoms about a substitutional impurity as compared with an interstitial. It should be noted that the second term in (20) will be of the same magnitude as the first in the case of impurities, and that it will be negative if the impurity atom is smaller than the surrounding atoms.

We must consider next the origin of the recovery processes that occur at low temperatures and which account for 50 percent of the resistivity increase due to damage at $-180°$C. It seems probable that most, if not all, of this recovery is due to the recombination of very close interstitial vacancy pairs, as has been suggested previously.[1] It is to be expected that such closely spaced pairs will be produced in large numbers by the irradiation since most of the damage is due to secondary and tertiary knock-ons whose initial energy is relatively small and is dissipated quickly to lattice vibrations.[2]

A few considerations will show that such an hypothesis can account easily for the observed behavior. Consider an interstitial atom in the body centered position of a unit cell. A vacancy at the face centers or corners of the same cell would probably not be stable. However, in the adjacent cells which have a face or an edge in common with the interstitial cell, there are 126 vacancy sites available, and these are of six different varieties. Furthermore, the lattice strains in this immediate vicinity are sufficiently large to lower the barrier heights several tenths of an ev. The annealing would therefore occur in several stages and a distribution in activation energies would result. The data in Figs. 3 and 4 are in accord with this view. More positive evidence is provided by Fig. 6, which indicates that the single process due to volume diffusion and annihilation is superposed on a background of other recovery processes. The striking feature is that the background disappears when the single process takes over, as would be expected of a transition from correlated annihilation to annihilation by true volume diffusion. On the other hand, this feature would be only a coincidence if the low temperature annealing were due to processes of an essentially different nature.

Finally, we must consider the resistance that remained after anneals at and above room temperature, which accounted for 25 percent of the total increase. At present one can only speculate about the nature of the lattice imperfections that are responsible. A possible explanation is that this damage is caused by thermal

[6] The author is grateful to Dr. J. D. Eshelby for pointing out the existence of this extra term.
[7] D. L. Dexter, Phys. Rev. **87**, 768 (1952).
[8] Ir. P. Jongenburger (to be published).
[9] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).
[10] R. E. Hoffman and D. Turnbull, J. Appl. Phys. **23**, 1409 (1952).

spikes which result from the energy loss of the bombarding particles and their knock-ons. This action causes a region along the path of the particle to be quickly melted and quenched, so that small disordered areas that would anneal only at recrystallization temperatures may result occasionally. Some of the residual resistance may be due to interstitials that were not annihilated as a result of vacancies being trapped at other lattice imperfections. Then, Eq. (8) would have to be replaced by

$$df/dt=-cf(f+\alpha), \tag{21}$$

where α is the initial concentration of vacancy traps. Since (21) resembles a first-order process if α is appreciable, the best value for n in (7) would have to have been closer to 1 if such processes were of major importance.

It is of interest to compare the annealing of damage due to irradiation with that due to cold work. Recent isothermal annealing experiments on copper that was cold worked at liquid helium temperature[11] have shown that recovery of the resistivity occurs in two temperature regions. In the vicinity of $-110°C$ an activation energy for recovery of 10.2 kcal/mole (0.44 ev) was found, and near $-30°C$ a value of 15.5 kcal/mole (0.67 ev) was found. These energies are almost identical with the values measured at the same temperatures in the present studies on irradiated specimens. These results suggest that there is some similarity among the imperfections produced by the two techniques.

Theoretical calculations[9,12] of the activation energies for the motion of interstitial atoms and vacancies in copper yield values around 1 ev. The present experiments, considered with those on quenching[3] and cold work,[4] indicate that the energy of 0.68 ev is to be associated with the motion of vacancies. The energy for interstitial motion cannot be less (and is probably greater), otherwise, the annihilation process would have been observed at lower temperatures. The observed activation energy for self-diffusion in copper[13] is 2.07 ev (47.7 kcal) and should be the sum of the energy required to produce a vacancy and the energy required for motion. One therefore obtains a value for the energy of production of a vacancy of 1.39 ev, which compares favorably with the calculated values[12] of about 1.5 ev.

VII. SUMMARY

The conclusions that can be drawn from this work fall into two categories, those that are experimental and hence factual and those that depend upon interpretation. In the first class we have the following:

1. Most, if not all, of the initial bending in the resistivity *versus* bombardment curve is due to thermal annealing that takes place at the temperature of the bombardment. Such effects are important even at liquid nitrogen temperatures.
2. Recovery below $-60°C$ is characterized by activation energies which vary with temperature and, therefore, can be described only by a number of thermally activated processes. The observed energy is approximately proportional to the absolute temperature and is 0.44 ev near $-100°C$. This recovery accounts for 50 percent of the total increase.
3. Recovery near $-30°C$ is characterized by a unique activation energy of 0.68 ± 0.02 ev and can be described by a mathematical equation of simple form, (7) or (9). This recovery accounts for 25 percent of the total increase due to damage at $-180°C$.
4. At room temperature 25 percent of the resistivity increase remains and does not anneal out below $+170°C$.
5. The resistivity increase due to radiation damage obeys Matthiessen's rule, at least to a good degree of approximation in the temperature region from $-125°C$ to room temperature.

The second class contains conclusions of various degrees of certainty and which may need modification or rejection upon further experimental evidence or theoretical consideration.

1. The low temperature annealing is due to the recombination of very close interstitial vacancy pairs. The low activation energies and their variation are due to lattice strains near the several varieties of vacancy sites about the interstitial atoms.
2. The recovery process above $-40°C$ is due to the volume diffusion of vacancies and their annihilation with interstitial atoms. For low concentrations of interstitials and vacancies the recombination follows an equation, (7), of the second-order reaction type.
3. Deviations of the recombination from a reaction rate of the binary type are due to the enhancement of the diffusion process as a result of lattice strains produced by the interstitial atoms. A rate of recovery results [Eq. (9)], which depends exponentially on the concentration of interstitials.
4. The energy of production of a vacancy is 1.39 ev and the energy of motion is 0.68 ev.

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