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Electrical Resistivity Study of Lattice Defects Introduced in Copper by 1.25-Mev Electron Irradiation at 80°K

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The electrical resistivity change produced in copper by 1.25-Mev electron irradiation at 80°K has been measured. The recovery of this change upon annealing has been studied. A recovery state centered near room temperature exhibited a phenomenological activation energy of 0.60±0.01 ev and obeyed a second-order chemical rate equation. It is proposed that this state is associated with the annihilation of interstitial atoms and vacant lattice sites resulting from interstitial migration. The present results are compared with those of other workers in an effort to understand the differences in the recovery of the electrical resistivity change produced by electron and cyclotron particle irradiation.

I. INTRODUCTION

IN the past, the main effort of studies in the field of radiation damage in metals has been devoted to the determination and understanding of the gross effects of fast particle irradiation. Such studies have become increasingly more quantitative in recent years, and have contributed considerably to the understanding of the nature of lattice imperfections in metals.[1] It is now possible, with appropriately chosen irradiation experiments, to produce certain types of defects, advantageous to the fundamental study of lattice imperfections. For example, low-energy electron irradiation can be used to produce a particularly simple distribution of point defects in metals, namely, equal numbers of interstitial atoms and vacant lattice sites (vacancies).

The defects produced in metals at low temperatures by electron irradiation can also be produced by such other means as cold work, quench from high temperatures, and irradiation with heavier particles. However, electron irradiation has the peculiar advantage that (providing the defects are immobile at the irradiation temperature) (a) the relative concentrations of interstitials and vacancies are known, (b) other defects such as multiple vacancies and dislocations are not produced, and (c) the distribution of the defects is homogeneous, as opposed to the clustering of defects which results from irradiation with heavier particles.[2] From these considerations, one might expect that electron irradiation experiments should provide one of the best means of checking theoretical calculations concerning the properties and behavior of interstitials and vacancies in metals.

The present work consists of a study of copper which was irradiated at liquid nitrogen temperature with 1.25-Mev electrons. The physical property used throughout the experiment as a measure of the damage was the electrical resistivity. An exposure curve, a tempering curve from 173° to 573°K, and an isothermal recovery curve at 293°K were obtained. Analysis of the data in the light of results obtained in other investigations led to the postulation of the model described in Sec. V.

II. EXPERIMENTAL

A wire, 0.016 inch in diameter and approximately 24 inches in length, was drawn from Johnson-Matthey 99.999% pure copper. This wire was wound on a mica-insulated copper frame and annealed in vacuum for $1\frac{1}{2}$ hours at 425°C. Current and voltage probes were soldered onto the specimen and were led out through a stainless steel tube connected to the frame. After initial electrical resistivity measurements were made (0.34×10^{-8} ohm-cm at 4.2°K), this assembly was placed in a special target box of an electron accelerator, as shown in Fig. 1. A pressurized storage tank provided a continuous stream of liquid nitrogen flowing through the target box, thus immersing the entire framework, with the exception of the specimen surface facing the electron beam. Since the diameter of the wire was an appreciable fraction of the range of 1.25-Mev electrons in copper, the specimen was irradiated in equal amounts from each side to insure uniform damage. In this manner, two 1.25-Mev electron irradiations were performed at 93°K. From the data of the first irradiation, a resistivity *vs* exposure curve and a tempering curve from 173° to 573°K were obtained; from the second, a room-temperature isothermal curve and an additional tempering curve for the 363° to 573°K temperature range were obtained. All resistivity measurements were made at 4.2°K, using standard potentiometric methods with a measuring current of 4.3 amperes. The relative experimental error in the resistivity measurements was approximately $\pm1.0\times10^{-12}$ ohm cm.

The available data on the recovery of the electrical resistivity in irradiated copper suggest that there are four major recovery regions. In this paper they will be denoted as follows: Region I, 12° to 50°K; Region II, 50° to 233°K; Region III, 233° to 373°K; Region IV, 373° to 573°K.

The exposure curve was determined by periodically stopping the irradiation and making helium point

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[1] For a recent review of this work see J. W. Glen, Advances in Phys. 4, 381 (1955).

[2] J. S. Koehler and F. Seitz, *Report of Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), pp. 222-231.

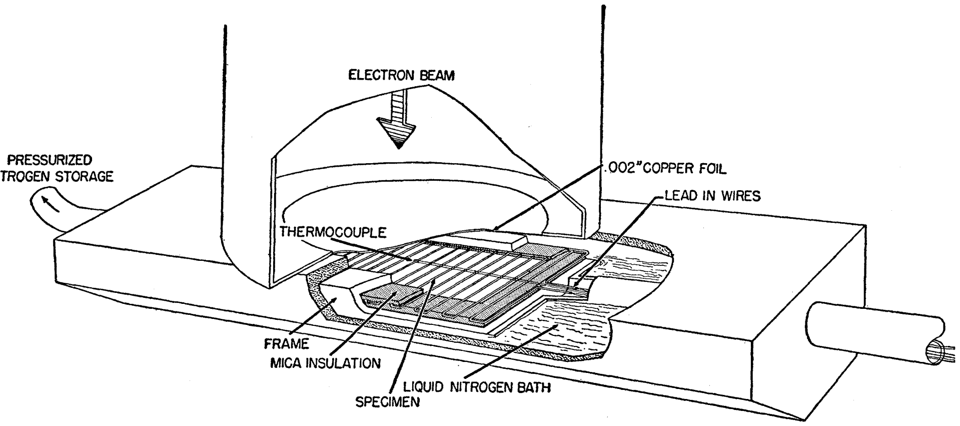

FIG. 1. Target box assembly for low-temperature electron irradiation.

resistivity measurements. The total integrated exposure was 2.7×10^{18} electrons/cm^2. The observed resistivity change as a function of integrated exposure is shown in Fig. 2. This specimen was then annealed for five minute periods in 15 degree intervals at temperatures between 173° and 573°K. The results of this treatment are illustrated in Fig. 3. The second specimen was irradiated to an integrated exposure of 3.4×10^{18} electrons/cm^2. Following the irradiation, the sample was annealed at 213°K for 10 minutes to remove the damage which recovers below the Region III state (see Fig. 3). The specimen was then annealed for various time periods at 293°K. Resistivity measurements were made after each period, the first being $1\frac{1}{2}$ minutes. These data are plotted in Fig. 4. After a total elapsed time of 1160 minutes at 293°K, this specimen was used to repeat the tempering curve of Fig. 3 in the temperature range 363° to 573°K. In an effort to isolate the recovery processes in this range, the heating rate used to obtain the data of Fig. 3 was reduced by a factor of 4.5; specifically, resistivity measurements were made after 15 minute anneals at each 10 degree interval. These results are shown in Fig. 5.

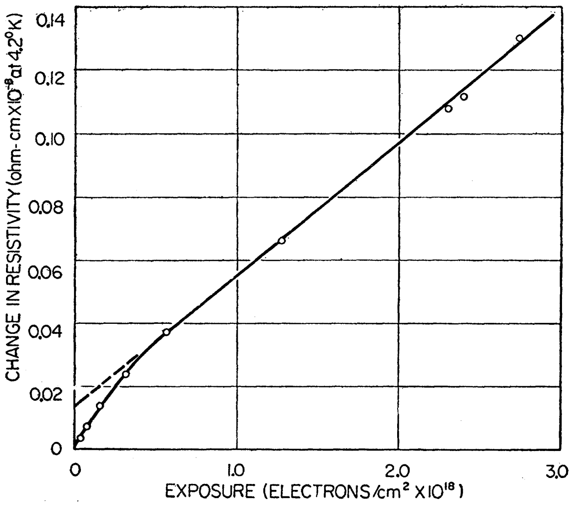

FIG. 2. Electrical resistivity changes in copper during a 1.25-Mev electron irradiation at 80°K.

In all of the above procedures, petroleum ether was used as the temperature bath below room temperature and Fisher Bath Wax for the higher temperatures.

III. METHOD OF ANALYSIS

A. Activation Energy Determination

The recovery of certain physical property changes in solids during annealing treatments is frequently observed to obey a rate equation of the form,

$$dp/dt=F(p,q_1,q_2,\cdots q_n)e^{-E/kT}, \qquad (1)$$

where p represents the property measured, t the time, T the absolute temperature, k the Boltzmann constant, and E the activation energy for the recovery process. The q's represent other variables, independent of t and T, whose significance will be described later. For a given recovery state (all of the property change associated with a given unique activation energy) it is generally believed that a particular kind of lattice imperfection is thermally excited and thereby induced to undergo a change such as migration to a position of lower energy, where its contribution to the measured

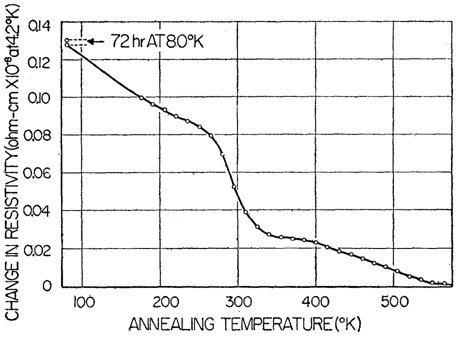

FIG. 3. Recovery of electrical resistivity of copper after 1.25-Mev electron irradiation at 80°K (heating rate—3°K/min).

property is altered. The activation energy, E, then represents the energy difference between the height of an "energy barrier" which must be overcome and the initial energy of the imperfection. Then the Boltzmann factor, $e^{-E/kT}$, represents the temperature dependence of the probability per unit time that the imperfection overcomes the barrier. The density of such imperfections in their initial state is denoted by n. The more basic rate equation should then be

$$dn/dt=f(n,q_1,q_2,\cdots q_n)e^{-E/kT}. \tag{2}$$

In order that Eq. (1) follow from Eq. (2), it is necessary to assume that the relationship between p and n is a single-valued monotonically increasing or decreasing function, independent of t, T and the q's,

$$p=g(n). \tag{3}$$

The q's, which depend on the previous history of the specimen, involve the spatial distribution of the sinks to which the imperfections must migrate, an example being the r_0 characterizing the spatial distribution of dislocations in a diffusion-type kinetics.[3] They can be constant or functions of n for specimens having identical history.

In general, Eq. (1) can be integrated as follows:

$$\lambda(p,q_1,q_2,\cdots q_n)\equiv\int_{p_0}^{p}\frac{dp}{F(p,q_1,q_2,\cdots q_n)}=\int_0^t e^{-E/kT}dt\equiv\theta, \tag{4}$$

where θ is referred to as the temperature-compensated time. For identical specimens (same history prior to annealing treatment), the q's need not be considered; thus for such specimens, the inverse function of Eq. (4) is

$$p=p(\theta). \tag{5}$$

Consider now two specimens with identical histories. The first specimen is to be annealed at a series of successively higher temperatures for equal time intervals; the temperature intervals need not necessarily be equal. A property, p, is measured at the end of each such temperature pulse. If the temperature coefficient of p is negligible or accurately known, measurements can be made at the temperature of each pulse. If not, after each pulse the specimen can be quenched to a standard base temperature, at which the recovery rate is negligible, for the purpose of making the measurements. During each pulse the temperature must be maintained constant. Let T_i denote the temperature of the specimen during the ith pulse, p_i the measured value of p after the ith pulse, θ_i the corresponding value of θ, according to Eq. (5), and t_i the total elapsed time at the end of the ith pulse.

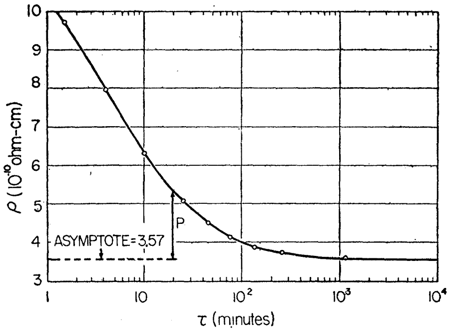

FIG. 4. Recovery of electrical resistivity during isothermal annealing at 298°K.

For a given pulse one can write

$$\Delta\theta_i\equiv\theta_i-\theta_{i-1}=\Delta te^{-E/kT}, \tag{6}$$

if the recovery is all characterized by a single activation energy, E, according to Eq. (1). Here,

$$\Delta t\equiv t_i-t_{i-1}=\text{constant}, \tag{7}$$

since, for the first specimen, the time intervals are all equal. Equation (6) can be written,

$$\ln\Delta\theta_i=C'-E/kT_i, \tag{8}$$

where $C'\equiv\ln\Delta t$.

The second specimen is to be annealed at a single temperature and the recovery of the property, p, measured as a function of annealing time. Let T_a denote the temperature of this isothermal anneal and τ the annealing time. The experimental p vs τ curve thus obtained with the second specimen can be used to determine the $\Delta\theta_i$ values to be used in Eq. (8) for the first specimen. From Eq. (4), it is seen that

$$\tau=\theta e^{E/kT_a}. \tag{9}$$

Let τ_i denote the value of τ corresponding to θ_i. Then

$$\Delta\tau_i\equiv\tau_i-\tau_{i-1}=\Delta\theta_i e^{E/kT_a}, \tag{10}$$

or

$$\ln\Delta\tau_i=\ln\Delta\theta_i+C'', \tag{11}$$

where $C''\equiv E/kT_a$. Substituting into Eq. (8), one

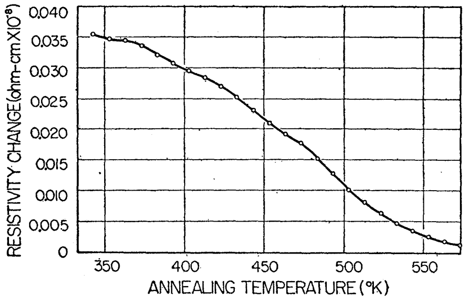

FIG. 5. Electrical resistivity recovery in Region IV.

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[3] Brinkman, Dixon, and Meechan, Acta Metallurgica 2, 38 (1954).

obtains

$$\ln\Delta\tau_i = C - E/kT_i, \qquad (12)$$

where $C \equiv C' + C''$.

For the general case described above, it is necessary that the two specimens have the same initial defect concentrations. However, there are cases, e.g., when the chemical rate equation,

$$dn/dt = -\nu n^{\gamma} e^{-E/kT}, \qquad (13)$$

is obeyed, where identical histories are not necessary. In the case where Eq. (13) is valid, the isothermal curves of two specimens with different initial defect concentrations will be identical, with the exception of a displacement of the origin, $\tau = 0$. Therefore, while the measured τ values will differ for two such specimens (by the amount by which the origin is displaced), the $\Delta\tau$ values will be the same, and Eq. (13) should still be valid.

From the p *vs* τ curve obtained with the second specimen, one can determine the τ_i corresponding to each p_i measured on the first specimen. The $\Delta\tau_i$ for each successive pulse, corresponding to the appropriate T_i, can therefore be determined, and by plotting $\ln\Delta\tau_i$ *vs* $1/T_i$, a straight line should result for each portion of the recovery associated with a unique activation energy. The slope of the straight line then determines the activation energy, according to Eq. (12). If the recovery resulting from annealing in a given temperature interval has more than a single activation energy associated with it, the $\ln\Delta\tau$ *vs* $1/T$ plot will exhibit straight-line segments in each interval in which only a single activation energy is effective, but will be curved in overlapping regions where two or more activation energies are governing the recovery. Therefore, the present method of analysis provides a more definite criterion than does the slope-change method used by Overhauser[4] for determining that portion of the recovery associated only with a unique activation energy. In addition, when the amount of recovery is small the present method permits one to determine the activation energy with greater accuracy, since it involves direct property rather than slope measurements.

B. Kinetics Determination

It may be possible to obtain a complete determination of the recovery kinetics of a state by a detailed analysis of the isothermal curve. If Eq. (13) is obeyed and the property p is proportional to the defect concentration n, then

$$p = R_D n, \qquad (14)$$

where R_D denotes the property change associated with unit defect concentration. Substitution of Eq. (14) into (13) gives

$$dp/p^{\gamma} = -K dt, \qquad (15)$$

where

$$K \equiv \nu R_D^{1-\gamma} e^{-E/kT}. \qquad (16)$$

If $\gamma \neq 1$, integration of Eq. (15) yields

$$p^{1-\gamma} = C(t+M), \qquad (17)$$

where $C \equiv K(\gamma - 1)$ and $M \equiv p_0^{1-\gamma}/C$. Here p_0 is the value of p when $t = 0$. If the chemical rate equation is valid, it will be possible to choose a positive value of M such that the plot of $\ln p$ *vs* $\ln(t+M)$ yields a straight line. Then, from Eq. (17), it is seen that the order of reaction, γ, can be determined from the slope of this line. The constant M represents the time which would be required for the defect concentration to be reduced, as a result of annealing at temperature T, from an infinite value to that value corresponding to p_0. Thus it is evident that M must always be positive.

In the following section, p will be defined as the difference between the resistivity change remaining at time, t, and the asymptote of the isothermal curve (see Fig. 4),

$$p = \rho - \rho_\infty, \quad p_0 = \rho_i - \rho_\infty, \qquad (18)$$

where ρ_∞ is the asymptote and ρ_i is the value of ρ when $t = 0$.

IV. DISCUSSION

A. Exposure Curve

An examination of the exposure curve of Fig. 2 shows a slight curvature in the initial portion. This curvature is believed to be dependent on either the geometry or purity of the specimen since the magnitude of the effect increased with decreasing diameter of the wire specimen. Therefore, it is not considered typical of pure bulk material. Except for this early portion, the exposure curve is linear within experimental error up to at least 3×10^{18} electrons/cm^2, corresponding to a resistivity change of 1.3×10^{-9} ohm-cm. The measured slope of this linear curve is 4.2×10^{-28} ohm cm per electron/cm^2.

It was pointed out in the Introduction that electron irradiation should produce only the simplest type of radiation damage, namely, single interstitials and vacancies. A given primary displacement collision should produce only one of each, and one or both of these defects must persist at the temperature of irradiation as evidenced by the resistivity change. The resistivity of a unit concentration of the persisting defects (whether they be interstitials, vacancies or interstitial-vacancy pairs) will be denoted by R_D and the cross section for production of such a defect by σ_D. Then the slope of the exposure curve, 4.2×10^{-28} ohm cm per electron/cm^2, is equivalent to the product $\sigma_D R_D$. The agreement of available theoretical values of σ_D and R_D with the above slope will be discussed in the next section.

The experimental error associated with the exposure curve is primarily due to the uncertainty in the measurement of the integrated electron flux. The relative

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[4] A. W. Overhauser, Phys. Rev. **90**, 393 (1953).

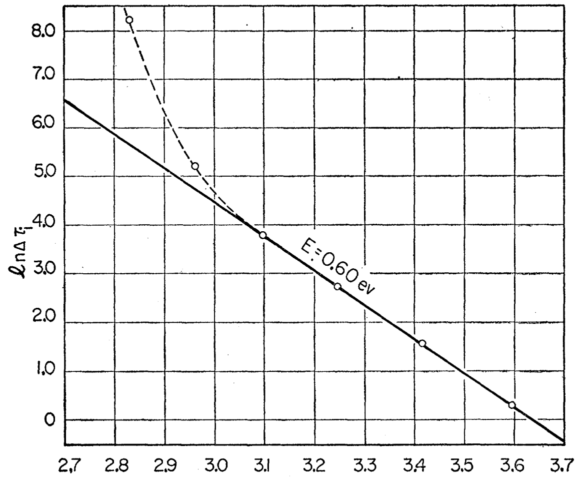

FIG. 6. Determination of activation energy for Region III.

uncertainty of the experimental points is estimated to be of the order of ±2%. Let us define a parameter β (analogous to that used by Cooper, Koehler, and Marx[5]) which is a measure of the curvature of the exposure curve,

$$dN=\alpha d\phi-\beta N d\phi, \tag{19}$$

where N is the number of defects per unit volume produced by the irradiation, ϕ is the integrated electron flux, and α is the number of defects produced per primary particle in unit distance. Since physical considerations lead one to expect positive nonzero values for β, an upper limit can be placed on the value of β from considerations of the experimental error. In this manner, the inequality, $0<\beta<10^{-19}$ cm^2/electron, has been deduced.

B. Region II

Approximately 30% of the induced damage recovers in a continuous manner in the temperature range 85° to 233°K. The recovery in this region appears similar to that studied by Overhauser,[4] with the exception that the amount of recovery is nearer 50% in the latter case. Overhauser found that this portion of the recovery is apparently characterized by a variable activation energy ranging from 0.2 to 0.6 ev.

C. Region III

An examination of Fig. 3 shows that approximately 50% of the induced resistivity change recovers in Region III. The rapid drop in the tempering curve in this region suggests the existence of a single unique recovery process. When the isothermal curve in Fig. 4 is combined with the tempering curve in the manner outlined in Sec. III, it is evident that nearly all of the resistivity which recovers in that region is associated with such a unique process. The activation energy for this process, as determined from the slope of the straight line portion of the curve in Fig. 6, is 0.60 ev, with a probable error of ±0.01 ev.

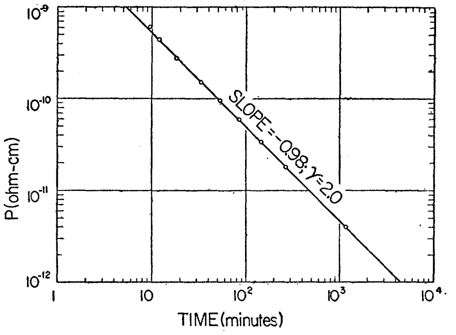

FIG. 7. Determination of reaction order (γ) for Region III, with $M=8$ minutes.

Following Eq. (17), ln$p$ has been plotted in Fig. 7 as a function of $\ln(t+M)$, with M equal to eight minutes. The resulting slope is -0.98 ± 0.03. Thus the chemical rate equation is obeyed within the experimental error with $\gamma=2.0$. From the values of M, γ, and p_0, K has been determined to be 1.6×10^6 (ohm cm sec)$^{-1}$. By using either experimental or theoretical values for R_D and the presently determined activation energy E, the frequency factor, ν, may then be determined from Eq. (16). For example, if R_D is taken as 5×10^{-4} ohm cm, ν is found to be 1.6×10^{13} sec^{-1}.

Overhauser has studied a similar recovery process in deuteron-irradiated copper. He found that the chemical rate equation was obeyed with $\gamma=2.5$ and $E=0.68$ ±0.02 ev. This state was centered at about 243°K, whereas the corresponding state from electron irradiation is centered at about 298°K. If these two states result from the same recovery process, one should be able to account for the differences in γ, E, and the center temperature (T_c).

Marx[6] has pointed out that a recovery process of a nonrandom distribution of defects which normally obeys the chemical rate equation should exhibit a reaction order higher than that expected for a random distribution. Since the defects produced by 12-Mev deuterons should be produced in clusters,[2] while those produced by 1-Mev electrons should be randomly distributed, Overhauser's value for γ should be expected to be higher than the presently determined value.

Unless a similar argument can account for the difference in the measured activation energies, this discrepancy cannot be resolved at present. However, this difference does not seem too serious, in view of the probable errors.

The shift of T_c can be accounted for on the basis of the relative values of the defect concentration produced by deuterons and electrons and the relative heating rates used in the two experiments. It is shown in

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

[6] J. W. Marx, Phys. Rev. **91**, 1564 (1953).

Appendix A that the center temperature of Overhauser's state should occur 63°K below that of the electron state, if the same process is responsible for the recovery. The actual temperature shift is approximately 55°K, indicating that this is the case. It should be noted that this is a violation of the often used hypothesis that the temperature at which a particular recovery state occurs is proportional to the activation energy.

D. Region IV

It is seen from Fig. 3 that approximately 20% of the resistivity change induced at 80°K recovers in Region IV. For purposes of discussing this recovery region, we shall consider the curve in Fig. 5 where the fine structure is shown in greater detail. Since no isothermal curves were obtained, unique determinations of recovery kinetics for any existing recovery states in this region are not possible. However, the existence of three inflection points, with positive values of $d^3\rho/dT^3$, indicates that there are at least three separate recovery processes associated with the recovery data of Fig. 5. Furthermore, it is apparent that the recovery in this region is quite different from that following irradiation with cyclotron particles,[7] which is primarily a single recovery state characterized by the activation energy for self-diffusion.

V. MODEL

In the preceding sections the experimental data and accompanying analyses have been presented without considering the nature of the detailed mechanism for each process. In this section, we shall attempt to correlate the results of the present study with those of other workers in an effort to choose a model which best represents the available data. Such a model should offer an explanation for the observed phenomena discussed in the preceding section and summarized in Tables I and II.

A. Region I

The following independent arguments can be offered against the assignment of interstitial migration to the Region I recovery in the noble metals.

1. Both electron and deuteron irradiation should produce interstitial atoms as well as vacancies in all of the noble metals. Huntington's calculations[8] indicate that interstitials should migrate at a lower temperature than vacancies in copper, and it seems reasonable to assume that this is the case for silver and gold, also. Further, it can be shown that when interstitials migrate, most of them should annihilate at vacancies (see Appendix B). From these considerations, it can be concluded that a larger resistivity change should be associated with the recovery state in which interstitials migrate than with the state in which vacancies migrate. Therefore, in view of the relative magnitudes of the resistivity changes in Regions I and III following deuteron irradiation, it is inconsistent to assign interstitial migration to Region I and vacancy migration to Region III for silver or gold.

TABLE I. Exposure curves.

Type of radiation	Element	Slope (ohm cm per particle/cm^2)	β (cm^2/particle)
12-Mev deuterons[a]	Cu	2.21×10^{-24}	4.3×10^{-18}
	Ag	2.63×10^{-24}	6.6×10^{-18}
	Au	3.79×10^{-24}	2.2×10^{-18}
1.25-Mev electrons	Cu	4.24×10^{-28}	$0<\beta<0.12\times10^{-18}$

[a] See reference 5.

2. The well-defined state observed in Region I in copper and silver following deuteron irradiation is absent in gold. Copper, Koehler, and Marx[5] have shown that the Z dependence of the damage rate, calculated by Seitz, fits their data quite accurately. If a well-defined state in gold, similar to the Region I state in copper and silver, occurs below the irradiation temperature of 12°K, then the observed Z dependence should not agree with the theory of Seitz.[9] Thus it seems improbable that such a well-defined state exists in gold, and therefore interstitial migration should not be assigned to the Region I recovery state for gold.

3. It was pointed out earlier that the exposure curve for electron irradiated copper near 80°K is linear within the experimental error. Since only interstitials and vacancies are produced by such irradiation, the observed linearity is expected (even if close interstitial-vacancy pairs are able to recombine) providing that both defects

TABLE II. Recovery.

	Approximate magnitude ($\Delta\rho/\rho_{\max}$)[a]					
	Deuteron irrad.			Electron irrad.		
Region	Cu	Ag	Au	Cu	Act. energy Cu	Kinetics Cu
I	50%	20%	0	Not investigated	Deut. irrad. 0.1 ev Not investigated for elect. irrad.	Not investigated
II	25%	35%	50%	30%	Apparently variable; range: 0.2–0.6 ev	Not a single unique process
III	15%	30%	35%	50%	Deut. irrad. 0.68 ev; elect. irrad. 0.60 ev	$dn/dt = \nu n^{\gamma}\exp(-E/kT)$ is valid; deuterons: $\gamma=2.5$; electrons: $\gamma=2.0$. Temp. shift of center of state =55°K
IV	10%	15%	15%	20%	1.0–2.1 ev	Elect. irrad: at least 3 different processes

[a] $\Delta\rho$ =resistivity recovery in particular region. $\rho_{\max}$ =total resistivity increase produced by irradiation at 12°K for deuterons and 77°K for electrons.

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[7] R. R. Eggleston, Acta Metallurgica 1, 679 (1953).

[8] H. B. Huntington, Phys. Rev. 91, 1092 (1953).

[9] F. Seitz, Discussions Faraday Soc. 5, 271 (1949).

are immobile at these temperatures. On the other hand, if interstitials can migrate at the temperature of irradiation, a curvature would be expected due to the migration and subsequent annihilation of interstitials at vacant sites.

A possible mechanism for Region I might be the recombination of those close interstitial-vacancy pairs having a particular geometry. It is not unreasonable to suppose that such a close pair is more stable in one of the noble metals than in another as a result of considerations of such factors as atomic size. Cooper *et al.* have pointed out that a considerably larger percentage of $\rho_{\max}$ recovers in gold than in copper or silver during the anneal in Region III, and that this difference is probably related to the absence of a Region I state in gold. This relationship might be that the particular close pair(s), which recombines in Region I in copper and silver, persists in gold until interstitials migrate. Interstitial migration could then initiate the recombination of these pairs, thus accounting for the large Region III state in gold.

B. Region II

Overhauser[4] assigned close pair recombination to this recovery following deuteron irradiation. Such an assignment can be seen to be inconsistent with the present results if one calculates the ratio of the number of close interstitial-vacancy pairs to the number of dispersed pairs for both electron and deuteron irradiation. A calculation based on conventional radiation damage theory shows that this ratio should be at least three times as great for electron irradiated copper as for deuteron irradiated copper (depending on the relative values which one assumes for the threshold displacement energy for production of close pairs and dispersed pairs). The ratio of the resistivity recovery in Region II to that in Region III for electron irradiation is about 0.6. Thus, the maximum value of this ratio for Overhauser's work is 0.2, if one assumes that all of the recovery which he observed in Region II is associated with close-pair recombination. Since his ratio is a factor of 10 greater than this, it seems that at least 90% of the recovery observed by Overhauser in this region must be associated with damage of a type not produced by electron irradiation.

At least two types of defects have been proposed which may account for this recovery. Van Bueren[10] has pointed out that pairs and groups of vacancies should be mobile in this temperature range. It has been shown[11] that such multiple vacancies should be produced by deuteron irradiation. Another type of defect which may be associated with this recovery is dislocation loops produced by displacement spikes. Again, these defects should be produced by deuterons but not by electron irradiation; they might also exhibit such a variable activation energy as Overhauser found. Thus, one or both of these mechanisms may be responsible for the major part of the recovery observed in Region II by Overhauser.

C. Region III

The preceding arguments have led to the following conclusions regarding interstitial migration in the noble metals: (1) interstitials should migrate at a lower temperature than vacancies, (2) the resistivity recovery associated with the state in which interstitials migrate should be at least as large as (and probably much larger than) the recovery associated with the state in which vacancies migrate, (3) interstitial migration should not be assigned to the Region I recovery, and (4) the recovery state in which interstitials migrate should be characterized by a second-order recovery kinetics.[12] Since these conditions are satisfied by the Region III recovery following both deuteron and electron irradiation, the most probable mechanism for this region seems to be interstitial migration and annihilation primarily at vacancies. The same assignment has been made in an earlier paper[3] and by other workers.[10,13,14]

D. Region IV

As indicated in Table II, about 20% of the induced resistivity change persists beyond Region III. Since no isothermal recovery curves were obtained in Region IV, the detailed kinetics remain uncertain. However, the tempering curves indicate that Region IV involves at least three separate processes. The second-order kinetics in Region III is obeyed accurately down to about 1% of the remaining defects. Thus, only a few percent (at most) of the induced interstitials and vacancies should persist as dispersed vacancies and multiple interstitials (platelets) after Region III. Therefore, it seems that the major part of the remaining 20% resistivity change must be associated with other interstitial and vacancy configurations which are formed during either the irradiation or the annealing preceding Region III.

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[10] H. G. Van Bueren, Z. Metallkunde **46**, 272 (1955).

[11] J. A. Brinkman, Am. J. Phys. (to be published).

[12] In chemical processes, the observed order of reaction is frequently depressed by unity from that characteristic of the number of constituents involved. This phenomenon arises when the concentration of reacting particles (interstitials and vacancies) is sufficiently high that a selection process occurs in which each interstitial is much more likely to be absorbed by its nearest neighboring vacancies than by those at somewhat greater distances. This leads to the development, as time passes, of a nonrandom distribution of interstitials with respect to the remaining vacancies. The condition which must be fulfilled in order that the expected reaction order be depressed by unity is that the average straight line distance, d, traversed by a migrating interstitial before encountering a stationary vacancy, must not be large relative to the average separation distance, s, between the two kinds of defects; i.e., $d/s\sim 1$. If $d/s\gg 1$, it is evident that the selection process is random and the interstitials continue to remain randomly located with respect to vacancies. In our case, simple order of magnitude calculations indicate that d/s lies in the range 10^2 to 10^3, indicating that the selection of vacancies by interstitials will be random, to a very good approximation. Thus, the reaction order should not be depressed from the expected second order.

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

[14] A. Seeger, Phil. Mag. **46**, 1194 (1955).

Whatever this configuration may be, the second order kinetics of Region III requires that approximately equal numbers of interstitials and vacancies be involved in the Region IV recovery. Possibly the initial curvature in the exposure curve is in some manner related to the recovery in Region IV. For example, the mechanism might involve the trapping of interstitials and vacancies by impurity atoms as they are produced by the irradiation, and the release of these trapped defects during the annealing in Region IV. The stated purity of the copper specimens (99.999%) allows a sufficient concentration of impurity atoms to trap enough interstitials and vacancies to account for the magnitude of the resistivity recovery in Region IV. If such a mechanism is operative, it could account for both the initial curvature of the exposure curve and the Region IV recovery.

E. Exposure Curves

Jongenburger[15] has calculated the resistivity per unit concentration of copper interstitials and vacancies to be 5×10^{-4} and 1.3×10^{-4} ohm cm, respectively. Since both of these defects are immobile at 77°K and are produced in equal numbers by irradiation, the defects D, introduced earlier, are interstitial-vacancy pairs and the corresponding resistivity R_D is 6.3×10^{-4} ohm cm. From this value and the slope of the exposure curve in Fig. 2, the cross section for production of an interstitial-vacancy pair by a 1.25-Mev electron is calculated to be 0.67×10^{-24} cm^2. Using conventional radiation damage theory and making the usual assumption that all atoms are displaced which receive more energy than the threshold displacement energy (~25 ev), one calculates a value of about 42×10^{-24} cm^2. This is seen to be higher than the above value by a factor of about 60. A similar procedure shows that this discrepancy is a factor of about 15 for the exposure curve for deuteron irradiated copper reported by Cooper *et al.* The latter work was carried out at about 16°K; however, deuteron irradiation at 77°K [16] gives a discrepancy of a factor of about 45. (If one uses the theoretical value for R_D calculated by Blatt,[17] the above discrepancy factors are reduced by a factor of 2.3.)

TABLE III. Recovery mechanisms.

Region	Type of irradiation	Defects recovering	E (ev)
I	Deuterons	Close interstitial-vacancy pairs	0.1
II	Electrons	Close interstitial-vacancy pairs	0.2–0.6
	Deuterons	Dislocation loops, multiple vacancies, and close interstitial-vacancy pairs	
III	Electrons	Interstitials and vacancies (via interstitial migration)	0.60
	Deuterons		0.68
IV	Electrons	Vacancies, multiple interstitials, trapped interstitials and vacancies, and platelets	1–2.1

Harrison and Seitz[18] have suggested that this discrepancy might be resolved by replacing the usual assumption of a unique displacement energy by the assumption that the probability that an atom is displaced varies from zero to unity as the energy transferred to the atom increases from the threshold displacement energy to some appreciably higher value. The possibility also exists that the theoretical values for the resistivities of interstitials and vacancies are too large; however, it is doubtful that they are in error to this extent.

VI. SUMMARY

The model discussed is primarily an extension of that presented in an earlier paper.[3] This extension consists essentially of interpretations of the present electron irradiation results and the deuteron irradiation recovery observed by Cooper *et al.* The significant features of the model are shown in Table III.

The only experimental evidence which appears to be contradictory to this model is the quenching experiment of Kauffman and Koehler.[19] Seeger[14] has pointed out that, in this quenching experiment, a majority of the equilibrium concentration of vacancies should have disappeared during the quench. He further points out that Lazarew and Ovcharenko[20] have performed a similar experiment with gold and obtained appreciably different results. Meechan and Eggleston[21] have interpreted high-temperature resistivity anomalies to be due to vacancies, and thereby deduced the formation energy of vacancies in both gold and copper. Their results differ significantly from the results of Kauffman and Koehler, but are in substantial agreement with the present model. In view of this evidence, we are inclined to agree with Van Bueren and with Seeger in the belief that the results of Kauffman and Koehler should be interpreted in terms of double rather than single vacancies.

The original calculations by Huntington[22] of the formation energy of vacancies in copper have recently been revised by Fumi.[23] His results and Huntington's calculation of the activation energy for vacancy migration are in good agreement with the present model. Huntington[8] has also calculated the activation energy for migration of interstitial atoms in copper, obtaining a value of approximately 0.2 ev. A possible explanation

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[15] P. Jongenburger, Nature **175**, 545 (1955).

[16] Marx, Cooper, and Henderson, Phys. Rev. **88**, 106 (1952).

[17] F. J. Blatt, Phys. Rev. **98**, 245 (1955).

[18] W. A. Harrison and F. Seitz, Phys. Rev. **98**, 1530 (1955).

[19] J. W. Kauffman and J. S. Koehler, Phys. Rev. **97**, 555 (1955).

[20] B. G. Lazarew and O. N. Ovcharenko, Doklady Akad. Nauk. S.S.S.R. **100**, 875 (1955).

[21] C. J. Meechan and R. R. Eggleston, Acta Metallurgica **2**, 680 (1954).

[22] H. B. Huntington, Phys. Rev. **61**, 325 (1942).

[23] F. G. Fumi, Phil. Mag. **46**, 1007 (1955).

for the discrepancy between this value and the 0.6 ev of the present model might be the following.

Fumi has pointed out that an analysis of the pressure-volume isotherm for copper[24] suggests that the repulsive energy per ion pair at distances appreciably smaller than the equilibrium separation may be somewhat larger than that estimated by adjusting the constants in a Born-Mayer type interaction potential (used by Huntington) to account for the observed elastic-constants. He concludes that the activation energy for vacancy migration estimated by Huntington is therefore probably too small. It would seem that calculations of the activation energy for interstitial migration should be even more sensitive to such an error in the interaction potential, since they involve extrapolation of the potential from the equilibrium separation to even smaller distances than those encountered in the case of vacancy migration. It does not seem unreasonable, therefore, that the activation energy for interstitial migration is a few tenths of an electron volt greater than the value calculated by Huntington.

APPENDIX A

If one assumes that the tempering curve can be approximated by a uniform rate of temperature rise, $T=At$, then Eq. (13) can be written as

$$dn/dT=-(\nu/A)n^2e^{-E/kT}. \tag{A1}$$

The inflection point is determined by setting

$$\left.\frac{d^2n}{dT^2}\right|_{T=T_c}=0:$$

$$E/kT_c^2=2(\nu/A)n_ce^{-E/kT_c}, \tag{A2}$$

where T_c is the temperature at which the inflection point in the tempering curve occurs (this is assumed equal to the center temperature of the state). An approximate solution for Eq. (A1) is

$$\frac{1}{n_c}=\frac{1}{n_0}+\frac{\nu T_c}{A(1+E/kT_c)}e^{-E/kT_c}, \tag{A3}$$

where n_0 denotes the total radiation-induced concentration of defects. Substitution of Eq. (A3) into Eq. (A2) yields

$$\frac{n_0\nu}{A}e^{-E/kT_c}=T_c^{-1}\left(\frac{2}{E/kT_c}-\frac{1}{1+E/kT_c}\right)^{-1}. \tag{A4}$$

Let n_{0e}, A_e, and T_{ce} denote the appropriate quantities for electron irradiation and n_{0d}, A_d, and T_{cd} the corresponding quantities associated with Overhauser's deuteron irradiation. By use of the experimental values,

$$R_Dn_{0e}=6.45\times10^{-10}\text{ ohm cm},$$
$$A_e=180°\text{K/hr},$$
$$T_{ce}=298°\text{K},$$
$$R_Dn_{0d}=1.96\times10^{-8}\text{ ohm cm},$$
$$A_d=6.7°\text{K/hr},$$

and Eq. (A4), T_{cd} is found to be 235°K. Thus, the center temperature of Overhauser's state should occur about 63°K below that of the electron state, if the same process is responsible for the recovery, and the recovery kinetics are the same in both experiments.

It should be noted that some differences in the recovery kinetics of deuteron and electron irradiated copper were observed. The most significant difference is in the order of reaction ($\gamma=2.5$ for deuterons; $\gamma=2.0$ for electrons). This difference can be explained qualitatively by the defect clustering which deuteron irradiation produces.[6] If this is the only significant difference in the recovery kinetics for the two experiments, the calculated value of the shift of T_c (63°K) should be considered a minimum value, since clustering should tend to lower the temperature of a given recovery state slightly (perhaps a few degrees).

APPENDIX B

We shall accept the results of Huntington's calculations,[8] which indicate that interstitials should migrate at a lower temperature than vacancies. It will be assumed that when interstitials migrate they can be destroyed or rendered immobile by only three processes: (a) annihilation at vacancies, (b) annihilation or trapping at dislocations, and (c) coupling with other interstitials. Let us denote by n_I and n_V the instantaneous interstitial and vacancy concentrations, respectively. Since at any given temperature interstitials migrate more rapidly than vacancies, the initial ($n_I=n_V$) rate at which interstitials are removed from the lattice by means other than direct interstitial-vacancy annihilation will generally exceed the corresponding rate of removal of vacancies. Therefore, one can write the inequality

$$n_V\geq n_I. \tag{B1}$$

Intuitively, it seems certain that

$$\sigma_{IV}\geq\sigma_{II}, \tag{B2}$$

where σ_{IV} and σ_{II} denote the cross section for capture of a migrating interstitial by a vacancy and an interstitial, respectively. Then the ratio of the probability that a given interstitial will annihilate at a vacancy, to the probability that it will couple with another interstitial is

$$n_V\sigma_{IV}/n_I\sigma_{II}\geq1. \tag{B3}$$

Since the recovery in Region III is characterized by a pure second-order kinetics, it almost certainly results

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[24] J. M. Walsh and R. H. Christian, Phys. Rev. 97, 1544 (1955).

from the migration of either interstitials or vacancies. The migration of more than a few percent of these defects to dislocations would cause an observable change in the reaction order. Since this is not observed, the probability that the defects migrating in Region III are captured by dislocations is small relative to the probability that they are captured by vacancies:

Case A.—Interstitials migrate in Region III:

$$n_V\sigma_{IV} \gg n_D\sigma_{ID}; \qquad \text{(B4)}$$

therefore from Eq. (B3) one concludes that interstitials are primarily captured by vacancies.

Case B.—Vacancies migrate in Region III, interstitials having migrated previously:

$$n_V\sigma_{VV} \gg n_D\sigma_{VD}. \qquad \text{(B5)}$$

Assuming that

$$\sigma_{ID} \approx \sigma_{VD},$$

and

$$\sigma_{IV} \gtrsim \sigma_{VV},$$

then

$$n_V\sigma_{IV} \gg n_D\sigma_{ID}; \qquad \text{(B6)}$$

therefore, the same conclusion concerning migration of interstitials can be drawn as in Case *A*.

Thus, whenever interstitials migrate, the majority of them should be captured by vacancies.

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Atomic Theory of Electromagnetic Interactions in Dense Materials*

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This theory develops a quantum analog of the classical electron oscillator model. It argues first that the Hamiltonian of long-wave excitations of matter is equivalent to that of an assembly of oscillators under very general assumptions. Next, these oscillators are coupled with the electromagnetic field oscillators and the normal modes of the coupled system are analyzed. The normal modes of longitudinal and transverse excitation have different spectra; the transverse frequencies depend strongly on the wavelength but the longitudinal ones do not. If the "longitudinal photons" are eliminated after the transformation to normal modes, the resulting Coulomb law has the dielectric constant in the denominator. The dielectric response law is expressed as a series of oscillations and also in terms of Van Hove's correlation function. Born-approximation theory of the collisions of fast charged particles with the assembly of normal mode (longitudinal and transverse) oscillators yields the same total cross section as Fermi's macroscopic theory. The transverse excitations include the Čerenkov radiation.

1. INTRODUCTION

THE dielectric constant ϵ of a material is a property relevant to electrodynamic phenomena in which the fields vary but little from one atom to the next. From an atomistic standpoint, ϵ has been interpreted by the classical model in which atomic electrons can perform forced oscillations about their equilibrium positions; no corresponding quantum mechanical theory seems to have been developed.[1]

This paper presents an atomistic theory of dielectric effects which considers three coupled quantum mechanical systems: an aggregate of atoms, the long-wave components of the electromagnetic field, and additional charged particles not included in the aggregate of atoms. The immediate aim is to rederive certain formulas of macroscopic electrodynamics, specifically: (a) the Coulomb interaction $e_1e_2/\epsilon r_{12}$ of charges in a dielectric and the equivalent equation $\operatorname{div}(\epsilon\mathbf{E}) = 4\pi\rho$, and (b) the probability of energy losses of a charged particle which was calculated macroscopically by Fermi, and, as a function of scattering angle, by Hubbard.[2a,b]

The macroscopic treatment of Coulomb interaction has proved quantitatively successful in the theory of donor levels in semiconductors,[3] even though applied to systems of the order of 100 A only. Inelastic electron collisions in solids have been the object of much recent work.[4] The energy loss spectrum in these collisions is clearly related to the dielectric constant $\epsilon(\omega)$ of each material by the Fermi theory, especially in the form

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[*] Supported in part by the Office of Naval Research and the U. S. Atomic Energy Commission.

[1] The quantum electrodynamics in a medium whose dielectric properties are characterized by a constant ϵ, but are not derived from an atomic model, has been developed by J. M. Jauch and K. M. Watson, Phys. Rev. **74**, 950 and 1485 (1948); **75**, 1249 (1949).

[2] (a) E. Fermi, Phys. Rev. **57**, 485 (1940); J. Hubbard, Proc. Phys. Soc. (London) **A68**, 976 (1955). (b) A theory with similar aims but with a different approach has been developed recently by D. A. Tidman, Nuovo cimento **3**, 503 (1956) and Nuclear Phys. (to be published).

[3] W. Kohn, Phys. Rev. **98**, 1856 (1955). I wish to thank Professor Kohn for calling my attention to this problem and for a discussion of his own approach to an atomistic theory of the interaction.

[4] See, for example, Marton, Leder, and Mendlowitz, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. 7, p. 183.