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Analysis of Low-Temperature Interstitial Migration Kinetics in Copper*

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A quantitative analysis of the recovery kinetics of stage I_E in copper is made following 2-MeV electron irradiation using dose-dependent temperature shifting. The doses considered range from about 3×10^{-8} to about 2×10^{-6} concentration of defects. Over this range the order of kinetics is found to increase with increasing dose from 1.2 to 1.6, with the higher value appearing to be an asymptotic value for increasing dose. The variation of the order of kinetics over this dose range is explained using nominal second-order kinetics influenced by excess vacancy concentrations produced by interstitial trapping by residual impurities. The functional dependence of the kinetics upon the initial concentrations of defects is demonstrated. A discussion of interstitial recovery behavior is extended for all doses in terms of the amount of damage remaining at the end of stage I. The results are also discussed in conjunction with several current annealing models.

I. INTRODUCTION

At the present time there are many basic questions unresolved regarding recovery behavior of irradiation-produced defects. One area of contention revolves around the absence[1] or presence[2] of a mobile defect in stage I. The presence of the mobile defect was challenged because of the discovery of substructure[3–7] in the I_D and I_E region which has been reported by several authors. Whether the defect is mobile in stage I or not, even the interstitial configuration itself is a point under serious debate. It is of vital importance that an understanding of these points relating to low-temperature recovery be achieved without which a full understanding of higher-stage annealing cannot be reached.

Involved intimately in the questions of the type of defect and its motion in stage I is the order of kinetics of the I_E substage. One way to experimentally determine the order of kinetics of this process is to study its behavior as a function of dose, since processes with orders of kinetics greater than 1 exhibit a shift in temperature with dose. The results of an experiment designed for high resolution of the resistivity-recovery processes are presented here. A quantitative analysis of the kinetics of the I_E process is presented and the results discussed in terms of defect recovery processes in stage I and higher-temperature recovery stages.

II. EXPERIMENTAL

The copper used as sample material in the present experiments was obtained from the Sigmund Cohn Corporation in the form of wire with a stated purity of 99.999%. For the results of Snead, Wiffen, and Kauffman (SWK) samples of diameter ~50 μm were wrapped in a zig-zag configuration with 30 legs having a total irradiated length of 70 cm. The sample was sandwiched between sapphire plates of 1 mm thickness and clamped to the sample block. After washing, the sample (mounted on the block) was annealed at 450°C for 90 min in a vacuum of 10^{-6} Torr or better. In the work on copper by Iseler, Dawson, and Kauffman[3] (IDK) the sample material was rolled into foil from 125-μm wire in an M-shaped configuration of thickness ~50 μm, and sandwiched between sapphire plates. This foil was 250 μm wide and had an irradiated length of 8.5 cm. Annealing of these specimens was identical with the above. Resistivity ratios of 535 for the foil and 425 for the wire samples were obtained with no surface scattering corrections.

A National Bureau of Standards calibrated platinum resistance thermometer for temperature monitoring and a wire wound resistor for use in heating the block were imbedded in the sample block with Wood's metal. The sample block was mounted in a helium cryostat purchased from Andonian Associates, Inc., and modified by the addition of a small secondary helium container to which the sample block was attached.[3] Helium level in the secondary container was controlled by varying the pumping rate on this container and thus regulating the transfer rate of liquid helium from the primary container. Heating and cooling of the sample was then controlled by use of this pumping arrangement in conjunction with the heater. Temperature control between 7 and 90°K could be maintained to ±0.01°K maximum deviation. The isochronal anneal pulses for the IDK work were of 30-min duration at temperature with 0.75°K temperature increments and were of 20-min duration with 0.50°K increments for the SWK runs.

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† Present address: National Laboratory, Upton, New York.

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[2] J. W. Corbett, *Electron Radiation Damage in Semiconductors and Metals* (Academic Press Inc., New York, 1966).

[3] G. W. Iseler, H. I. Dawson, and J. W. Kauffman, *Lattice Defects and Their Interactions*, edited by R. R. Hasiguti (Gordon and Breach Science Publishers, Inc., New York, to be published).

[4] A. V. Granato and T. G. Nilan, Phys. Rev. 137, A4, 1250 (1965).

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[6] G. W. Iseler, H. I. Dawson, A. S. Mehner, and J. W. Kauffman, Phys. Letters, 17, 212 (1965).

[7] J. A. Tesk, E. C. Jones, and J. W. Kauffman, Phys. Rev. 133, A288 (1964).

An average time of 15 min elapsed between 4.2°K, the measuring temperature, and the attainment of the desired anneal temperature with approximately a 3-min interval between the temperature of the previous anneal and the desired temperature.

Electron irradiation of the samples was accomplished using the 2-MeV Northwestern University Van de Graaff accelerator. The beam was scanned with horizontal and vertical ac triangular signals, typically 280 and 2000 cps, applied to a conventional television yoke coil. The central portion of the scanned beam was selected using split collimators set to pass the desired sized and shaped portion of the beam. Uniformity of the beam is enhanced by overscanning the collimators and using only the central 20% of the total beam. Measurement of the changes in resistivity of the specimens due to the defects produced by irradiation below 10°K was accomplished by conventional potentiometric techniques. Precision of the measurements was $\pm 3\times 10^{-13}$ Ω cm for an uncertainty of $\pm 1\times 10^{-8}$ V in the emf for the IDK runs and $\pm 3\times 10^{-14}$ Ω cm for an emf uncertainty of $\pm 1\times 10^{-7}$ V in the SWK case.

III. EXPERIMENTAL DETERMINATION OF I_E KINETICS

Determination of the annealing kinetics of I_E using dose-dependent temperature shifting of the peak is made difficult due to the proximity of the I_D peak(s) and to the actual "overlap" in the recovery of these two substages. Corbett, Smith, and Walker[8] concluded from their dose-dependency analysis of I_E in copper following 1.4-MeV electron irradiation that the kinetics were bimolecular within their experimental error.

Bauer and Sosin[9] compared the values for the temperature shifts obtained from the data of Corbett *et al.* with calculated values for second order kinetics and found the calculated shifts larger than the measured ones. This can be interpreted as an effective order of reaction less than two (see Table I). Later work on I_E kinetics in copper by Granto and Nilan[4] using stored energy measurements following 11-MeV deuteron bombardment confirmed second-order kinetics within experimental error (not stated explicitly). Third order was ruled out in this work.

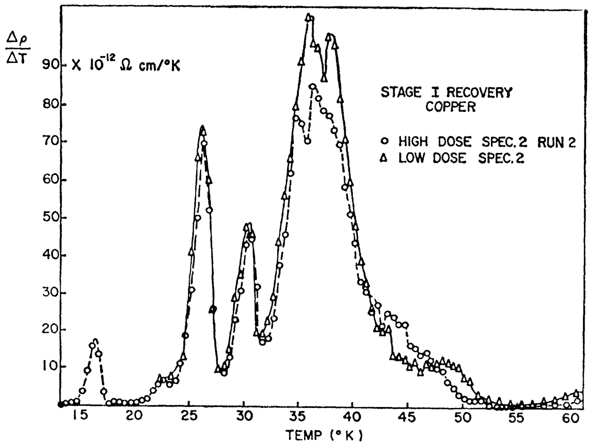

FIG. 1. High- and low-dose recovery of stage I in copper. Curves normalized to the amount coming out over 40–55°K range. Damage induced by 2-MeV electron irradiation. Doses: high dose 12.4×10^{-10} Ω cm, low dose 1.34×10^{-10} Ω cm.

TABLE I. Dose dependence of I_E in copper.

Run	$\Delta\rho$ Total (10^{-10} Ω cm)	ΔT_c (°K)	γ_{eff}	% out at 56°K
Low dose	1.34	···	···	75.9
Low dose[a]	4.9	0.50	$1.18\left\{\begin{matrix}+0.09\\-0.13\end{matrix}\right.$	87
Medium dose[a]	6.75	1.00	$1.30\left\{\begin{matrix}+0.16\\-0.10\end{matrix}\right.$	87
High dose 1	11.7	2.10	$1.57\left\{\begin{matrix}+0.15\\-0.05\end{matrix}\right.$	83.6
High dose 2	12.4	2.00	$1.55\left\{\begin{matrix}+0.15\\-0.05\end{matrix}\right.$	84.0
High dose[a]	38.4	2.95	$1.55\left\{\begin{matrix}+0.16\\-0.08\end{matrix}\right.$	86
Low dose[b]	3.0	···	···	85
Medium dose[b]	18.0	2.0	1.66[c]	88
High dose[b]	55.0	4.0	1.80[c]	85

[a] Data of Iseler *et al.* (IDK), (Ref. 3).
[b] Data of Corbett, Smith, and Walker for 1.4-MeV electron irradiation from Bauer and Sosin, Phy. Rev. **136**, 225 (1964).
[c] Error estimate not available.

The high-sensitivity sample/measurement configuration and the closely spaced points of the annealing schedule were chosen for a high precision in the measurement of resistivity changes and to give an accurate definition of the curves of the resistivity recovery rate. A very low defect concentration was required to shift the I_E peak to as high a temperature as possible, giving a separation of the I_D and I_E recovery region.

Figure 1 shows the low-dose resistivity recovery rate curve plotted along with a higher-dose curve. The good definition of I_E is evident in the low-dose case. In the following analysis all the recovery derivative curves have been normalized to the amount of resistivity recovering in the I_E region (40–55°K) for comparison. The dose-dependent temperature shift ΔT_c is obtained in the following way: We designate the center temperature of the low-dose I_E peak as T_{c1} and for the high dose as T_{c2}. From the I_E peak obtained from the low-dose derivative curve (Fig. 2) T_{c1} is well defined as is the high-temperature side of the peak. For complete definition of the peak, the low-temperature side is assumed to be not much different than the mirror image of the high-temperature side reflected through T_{c1} (dashed curve in Fig. 2). This procedure gives the position and shape of the I_E peak for the low-dose case.

This peak is now subtracted from the low-dose curve leaving, presumably, a dose-independent low-dose curve. Since the curves for the two doses to be compared have been normalized, if this dose-independent

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[8] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. **114**, 1460 (1959).
[9] W. Bauer and A. Sosin, Phys. Rev. **136**, 255 (1964).

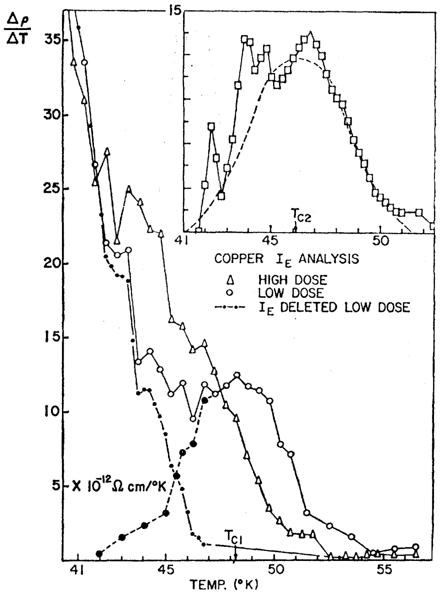

FIG. 2. Analysis of dose-dependent temperature shift of I_E in copper. Data points in inset represented by squares obtained by subtracting "I_E deleted low dose" curve from "high-dose" one. Dotted curve in inset is smooth fit to low-dose I_E peak.

part of the low-dose curve is subtracted from the high-dose derivative, only the dose-dependent part(s) of the high-dose curve remains. This remainder can then be fitted with the I_E peak obtained from the low-dose curve to obtain the center temperature T_{c2} of the high-dose peak. In this manner the shift in peak center temperature or ΔT_c is calculated. The effective order of kinetics defined by the temperature shift is then found from chemical rate theory using the relation

$$\Delta T_c \cong (\gamma_{\mathrm{eff}}-1)\frac{T_{c1}T_{c2}}{E/k}\ln\frac{n_{02}}{n_{01}}, \tag{1}$$

where γ_{eff} is the effective order of the kinetics, E the activation energy, K Boltzmann's constant, and n_{02} and n_{01} the concentration of defects annealing in I_E for high and low doses, respectively. The value used for E is 0.12 eV.[8]

The above procedure is based upon recovery rate curves produced by joining the data points by straight lines. A smooth curve is used only when fitting the low dose I_E to the remainder from the high-dose curves (see inset of Fig. 2). In considering the sources of error in this type of analysis, the most important is in the fitting which defines T_{c2}. The estimated error in T_{c2} is obtained from the "worst fits" for high- and low-temperature values of T_{c2}. Of less importance is the uncertainty associated with the value for n_{02}/n_{01}. Results of this analysis are listed in the top portion of Table I. The salient feature of Table I is the behavior of γ_{eff} with changing dose. The values all lie between 1 and 2 and decrease with decreasing dose. The values obtained from the data of Corbett *et al.* by Bauer and Sosin which are listed in the lower portion of the table are in agreement with this behavior.

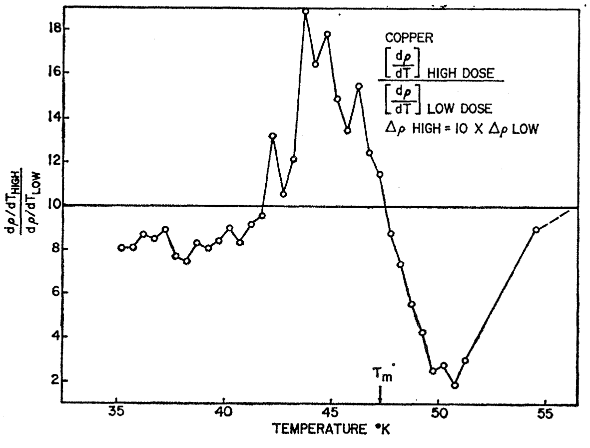

FIG. 3. Ratio of the isochronal slopes of the high and low doses of Fig. 2 as a function of temperature. Error in points above 55°K is large due to small recovery.

There is some independent corroborative evidence in the present work for kinetics of order less than two using a plot of the ratio of the recovery rates of the high and low doses as a function of temperature.[10] Any differences in the rates due to dose dependence will show up as a deviation from the ratio ordinate 10, this being the ratio of total damage over the range of interest for high and low doses. For a single peak shifting in temperature a characteristic serpentine curve is predicted with positive deviation on the low-temperature side. The results of such a plot are shown in Fig. 3 which shows the serpentine curve mentioned above. Information of a more quantitative nature is available, however, from the intercept of the curve with the line $[d\rho/dT]_2/[d\rho/dT]_1=10$ between the positive and negative portions of the curve. This intercept defines the temperature T_m that lies exactly halfway between T_{c1} and T_{c2}. (This is true to the extent that the derivative peaks are symmetrical about their respective center temperatures.) Since from Fig. 2 we obtained T_{c1}, then

$$\Delta T_c = T_{c1} - T_{c2}(T_{c1} - T_m).$$

Since $T_m = 47.4\pm0.2$°K with the error estimated from the graph, $\Delta T_c = 1.7\pm0.4$°K. This is to be compared with the value $\Delta T = 2.1_{-0.2}^{+0.4}$°K obtained from Table I for high dose No. 1. This check on the value of the temperature shift appears to be in good agreement with the previously obtained value. This same check applied to several of the other doses gave comparable results.

The results presented in this section demonstrate the effective order of kinetics of I_E to be substantially less than second order and to dose-dependent, decreasing with decreasing dose for comparisons with the same low-dose case.

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IV. ANALYSIS OF I_E KINETICS

In order to shift the I_E peak out of the I_D region it was necessary to employ low defect concentrations. If this concentration of defects approaches the concentration of residual impurity atoms (nominally 1×10^{-5}), then impurity trapping of a substantial number of the freely migrating interstitials may affect the order of kinetics of that process. The impurity-trapping phenomenon has been investigated in several metals.[11–13] Damask and Dienes[14] have treated the problem of interstitial-vacancy recombination with concurrent impurity trapping using chemical-rate theory. For various concentrations of interstitial-vacancy pairs relative to the residual impurity concentration, the concentration of the vacancies at the end of the I_E free migration substage is considered. For initially equal vacancy and interstitial concentrations i_0, initial impurity trap concentration I_0, C the concentration of interstitial-impurity complexes and V_1 the concentration of vacancies remaining at the end of the annealing stage in which the interstitial is mobile, then

$$V_1=\frac{I_0 i_0}{I_0+i_0}. \tag{2}$$

This assumes that the interstitial capture cross section of impurities and vacancies is the same. For differing interstitial concentrations the following conditions obtain

(a) $V_1=C=I_0$ for $i_0\gg I_0$,
(b) $V_1=C=i_0$ for $i_0\ll I_0$,
(c) $V_1=C=I_0/2$ for $i_0=I_0$.

For case (a) corresponding to high relative doses, I_E recovery starts out with equal concentrations of interstitial and vacancies with an excess of vacancies increasing from zero to a value of I_0 as the recovery proceeds. Since the number of excess vacancies throughout and at the end of the annealing process is small compared with the total number of vacancies being annihilated, the kinetics at the end of the annealing stage will be almost identical with the kinetics at the onset. In case (b), corresponding to very low relative doses, the excess vacancy concentration plays a much more active role in the determination of the recovery kinetics. As the recovery begins the kinetics are identical with those of case (a). Because of the higher probability of an interstitial encountering an impurity and being trapped rather than annihilating a vacancy, the excess vacancy concentration rapidly increases as the time progresses resulting in the order of kinetics rapidly approaching 1 [see Eq. (4)]. Since the order is changing over a portion (or over the entire) peak, the process is described by an average or effective order of kinetics. In case (b) this effective order would be close to 1 whereas in case (a) it would be closer to 2. Case (c), corresponding to comparable concentrations of impurity atoms and interstitials, is intermediary of (a) and (b) and more complex. The recovery begins with the kinetics of case (a). Excess vacancies due to the trapped interstitials increase in number but not as quickly or in as large relative numbers as in case (b). The kinetics then decrease throughout the annealing to some final value determined by the initial concentrations.

The order of kinetics γ is given by the expression

$$\frac{dn}{dT}=-\frac{K}{a}n^{\gamma}e^{-E/kT}. \tag{3}$$

But it can be shown[9] that for an initial excess concentration of vacancies, the recovery of interstitials should be governed by an expression having the form

$$\frac{dn}{dT}=-\frac{K}{a}(n^2+nV_{\text{ex}})e^{-E/kT}, \tag{4}$$

where $V_{\text{ex}}=\text{const}$ is the initial vacancy excess and γ as defined in (3) is a constant. However, in the case of concurrent impurity trapping V_{ex} is initially zero and increases as some function of the initial concentration of interstitials and impurities as the recovery progresses. Thus $V_{\text{ex}}=\text{const}$ in Eq. (4) then becomes

$$V_{\text{ex}}=f(i_0,I_0,T,t), \tag{5}$$

which means that in (3)

$$\gamma=\alpha(i_0,I_0,T,t). \tag{6}$$

In describing the recovery peak and its center temperature, some average of this quantity over temperature and time is necessary giving a quantity γ'_{eff}. The order of kinetics, then, which is determined by a dose-dependent temperature shift is a further average of the γ'_{eff} of the two I_E peaks under scrutiny, the γ'_{eff} being different for each dose. This average which is experimentally measured is the γ_{eff} of Eq. (1). If in Eq. (3) we substitute γ'_{eff} for γ, an expression for the temperature shift with changing dose is given by

$$\Delta T_c \cong \frac{T_{c1}T_{c2}}{E/k}\ln\left[\frac{\gamma_2'{}_{\text{eff}}\, n_{02}{}^{(\gamma_2'{}_{\text{eff}}-1)}}{\gamma_1'{}_{\text{eff}}\, n_{01}{}^{(\gamma_1'{}_{\text{eff}}-1)}}\right]. \tag{7}$$

For case (b) at the beginning of the section, the effective order can be described by the excess vacancy concentration and is obtained from Fig. 4 and listed in Table II. Figure 4 gives the effective order of kinetics for an initially second-order process with an initial concentration of excess vacancies present. The excess

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[11] T. H. Blewitt, R. R. Coltman, C. E. Klabunde, and T. S. Noggle, J. Appl. Phys. **28**, 639 (1957).

[12] C. L. Snead, Jr. and P. E. Shearin, Phys. Rev. **140**, 1781 (1965).

[13] A. Sosin and H. H. Neely, Phys. Rev. **127**, 1465 (1962).

[14] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach Science Publishers, Inc., New York, 1963).

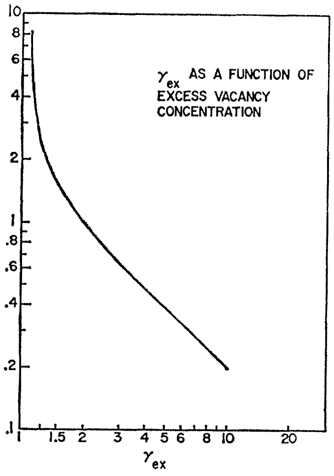

FIG. 4. The effective order of kinetics for a single normally second-order annealing process with initially unequal concentrations of reactants. n_{02} is the initial concentration of vacancies and n_{01} that for interstitials that are free to migrate (after Damask and Dienes, Ref. 14). Ordinate is ratio n_{02} to n_{01}.

vacancy concentration is estimated on the basis of the amount of damage unrecovered at the end of stage I as a function of dose (see Fig. 6). Note the low values obtained for γ_{ex} for all doses in Table II. These values are obtained for an *initial* excess vacancy concentration V_{ex} and do not correspond to the process here. Here the vacancy excess is zero initially and increases with the progression of recovery. By using the V_{ex} at the end of the recovery process, we have overestimated the average excess vacancy concentration over the recovery stage, thus obtaining lower values for the order of kinetics than measured. For the lower doses the error is seen to be less indicating the final vacancy excess approximation to be not as bad as in the case of high doses. This is exactly the kind of behavior expected due to the impurity-trap mechanisms for the cases where $I_0 \gg i_0$ [case (b)]. In this case trapping is highly probable with the excess vacancy concentration being established early in the recovery process. For the higher doses, the excess is obtained relatively more slowly, with the vacancy excess affecting most strongly the latter portion of recovery.

The values for γ_{eff} in the Corbett data (Table I) are higher than the ones obtained in the present work. This is due to a higher initial concentration of defects in their low dose causing γ'_{eff} of that dose to be higher than the one used for the low dose here since the low dose is the base from which γ_{eff} is calculated. The γ'_{eff} of the Corbett low dose should lie near the values obtained from Table II for the medium or low doses of IDK, making the values in Table I of γ_{eff} consistent.

TABLE II. γ_{ex} as a function of V_{excess} after Fig. 4.

	Total defect concentration[a]	$i_0(I_E)$	$\frac{n_{02}}{n_{01}}$	γ_{ex}
High dose (SWK)	4.65×10^{-6}	4.8×10^{-7}	2.6	1.22
High dose (IDK)	15.3×10^{-6}	1.73×10^{-6}	2.2	1.30
Medium dose (IDK)	2.7×10^{-6}	2.45×10^{-7}	2.5	1.23
Low dose (IDK)	1.94×10^{-6}	1.35×10^{-7}	3.1	1.18
Low dose (SWK)	5.35×10^{-7}	2.85×10^{-8}	5.7	1.10

[a] $\rho_{F.P.}=2\times10^{-4}$ Ω cm; $I_0=3\times10^{-7}$.

Since the concentration of excess vacancies present at the end of recovery in I_E is dose-dependent with the higher concentrations occurring for lower doses, the amount of damage remaining due to trapped interstitials is relatively higher for lower doses. Recovery peaks associated with release of interstitials from impurity traps should then show a dose dependence in the percentage of damage recovered, with higher percentages at lower does. We have investigated the peak labeled II_a by Sosin and Neely[13] in some detail. Figure 5 shows the results of this investigation. The peaks plotted here are all normalized to the amount of total damage. Note the absence of any temperature shift due to either dose or energy change. When compared on the basis of total damage introduced at helium temperature, it is found that twice as much recovery takes place in II_a for the low dose than in the high dose. This is in keeping with the lower percentage of I_E annealing found in the low dose.

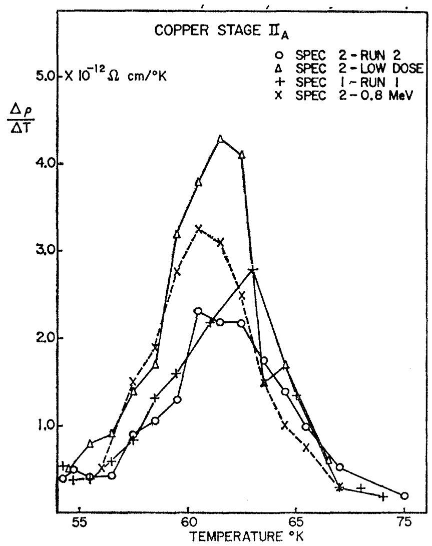

FIG. 5. Isochronal derivative curve of II_a substage in copper. Specimen 1, Run 1 and Specimen 2, Run 2 were irradiated to the same total dose of $\Delta\rho=12\times10^{-10}$ Ω cm. Low dose was a factor of ten lower. Normalization is to total damage for the high dose.

This decrease in I_E recovery with decreasing dose is quite evident in Fig. 6. Here the amount of resistivity recovered at 56°K is plotted as a function of dose. Note the increase of recovery in stage I with increasing dose as is expected from the behavior predicted by conditions (a), (b), and (c) of Eq. (2). From this curve an estimate of the concentration of trapping sites I_0 recovery can be made. Case (a) is realized in Fig. 6 for high doses that correspond to recovery of about 80% and above. Case (b) would correspond to a plateau type region similar to that of (a) but lying below the 60% recovery mark. Somewhere between those two regions is the region where i_0 is comparable with I_0 and the slope of the curve has its greatest value. An inflection point in the curve (not defined by the present limited data) would correspond to $i_0=I_0$. A good guess would appear to be a concentration corresponding to 70% stage-I recovery corresponding to an impurity concentration of $\sim 3\times 10^{-7}$. This estimate also has inherently another source of error in that the resistivity per Frenkel defect must be employed to estimate i_0. We use a value of $\rho_{\mathrm{F.P.}}=2\times 10^{-4}$ Ω cm/unit concentration. The estimate of I_0 is less than the nominal value for impurity concentration of 10^{-5}. This nominal value checks well with measurements of pre-irradiated residual resistivity.

V. DISCUSSION

The results of this paper have shown the kinetics of the I_E recovery substage in copper to be varying with dose and significantly less than second order. The analysis presented above has shown that over most of the dose range used in this work this behavior can be explained using a model in which interstitials are trapped as well as annihilated during their free migration in I_E. While the analysis was carried out in terms of impurity atoms being wholly responsible for the trapping mechanism, it is also likely that other traps, for example dimer formation or dislocations, make a contribution. It was shown that impurity trapping of the migrating interstitial produced an excess of vacancies which depend upon the concentration of impurities, concentration of interstitials at the beginning of the free migration process, and the extent of the recovery for that process. For all doses for which the condition $i_0 \gg I_0$ is not satisfied, the free migration recombination begins with kinetics of second order and decreases throughout the recovery process due to the presence of the above excess vacancies. The order of kinetics is continually changing over the course of recovery. Thus, an effective order of kinetics for the recovery peak will be some average of this changing quantity over the entire process and will take on a value between 1 and 2 depending upon the ratio of interstitial and trap concentrations.

The initial order of kinetics is either second order if the interstitial moves randomly in three dimensions as does the ⟨100⟩ split type or perhaps second or third order if it is of the ⟨110⟩ split or crowdion type.[14,15] Values for the effective order of kinetics taken from Fig. 4 are based upon the initial order of kinetics being 2. If initial third order is considered, Fig. 4 is altered by the raising of the curve and thus giving values of γ_{ex} too high for agreement with the experimentally determined ones, with the high-dose values greater than 2. Since the values for γ_{eff} in Table I appear to be approaching some value less than two for increasing dose, initial third order is ruled out as inconsistent with the present results. That the values for the order of kinetics γ_{eff} or γ'_{eff} are not expected to increase to very much higher values with increasing dose is predicted from the behavior of the curve showing the damage remaining at the end of stage I as a function of dose (Fig. 6). This curve appears to be leveling off at the doses used here indicating an excess vacancy concentration being achieved during the annealing process independent of dose over this higher-dose range. This leveling off with higher-dose over this dose range is very evident in a similar plot of damage remaining versus dose for silver.[16]

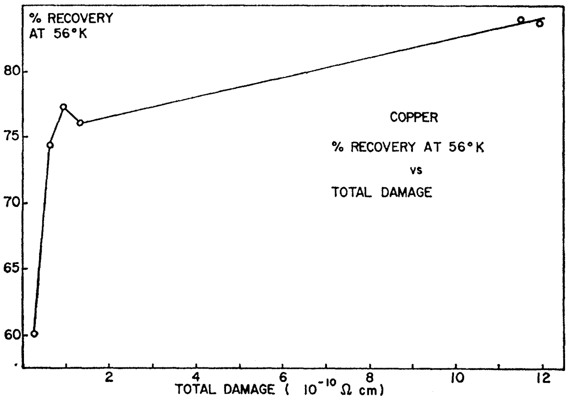

FIG. 6. Percent of recovery in copper at 56°K as a function of total damage from 2-MeV electrons.

In Fig. 7 we plot the percentage of resistivity recovering in stage I as a function of initial irradiation-induced resistivity similarly to Fig. 6, but extending the dose range beyond that of the present work and including data of other authors.[3,17] That complete recovery of

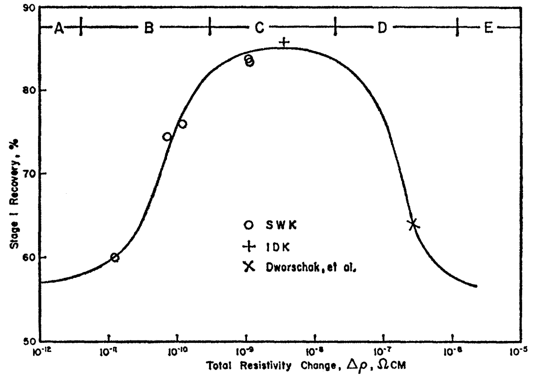

FIG. 7. Percent of stage I recovery as a function of total change in resistivity due to electron bombardment. Dworschak *et al.* datum for 3 MeV. All others for 2 MeV.

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[16] F. W. Wiffen, C. L. Snead, Jr., and J. W. Kauffman (to be published).

[17] F. Dworschak, J. Newhauser, H. Schuster, J. Wurm, S. Potyka, G. Sokolowski, and H. Wollenberger, Phys. Rev. Letters **16**, 685 (1966).

electron damage is not realized in stage I was recognized early and an explanation for the doses then under consideration to account for the unrecovered damage was put forward in terms of interstitial agglomeration during free interstitial migration.[8] This process, we believe, is dominant in region C of Fig. 7 in agreement with the above. It has been shown that impurity trapping is responsible for the majority of the damage remaining when the condition $I_0 \gtrsim i_0$ is met, this corresponding to regions A and B. When $I_0 \gg i_0$, then I_E is completely suppressed, only close pairs contributing to stage-I recovery and a plateau region of dose independency in the curve is achieved which we have labeled region A. Thus as the dose progresses from the plateau region of A where impurities completely dominate to the plateau region of C where the impurity influence has virtually disappeared, the total recovery of stage I shows a continual increase very similar to the increase of I_E kinetics over this same dose range. The connection between the two as discussed before with reference to the kinetics is related to the excess vacancy concentration present.

In region C where only the lower dose portion has been investigated using electrons and where $i_0 > I_0$ and interstitial-vacancy recombination is more probable than impurity trapping during free migration, the mechanism of dimer formation is invoked to account for the damage remaining. This process yields the same percentage of recovery due to interstitial-vacancy recombination and to dimer formation during free migration independent of defect concentration. Thus a plateau region is seen in the region corresponding to dimer formation, to the extent that higher complex formation is negligible, and to the extent that the ratio of close Frenkel pairs to uncorrelated pairs remains fixed at irradiation. This latter criterion does not hold for doses sufficiently high that the interaction between interstitials produces "overlap" of the spheres of influence of the interstitial defects. This overlap produces interstitial close pairs during irradiation similar to Frenkel close pairs. Such interstitial close pairs should, through their attractive interaction, possess an activation energy lying in stage I for the production of dimers. At this point in increasing dose where overlap begins then, dimers are formed at the expense of uncorrelated pairs to the larger extent and close Frenkel pairs to a lesser extent. This process is also a dose-dependent one, increasing in effect as the probability for overlap increases, producing a decrease in stage-I recovery with increasing dose.

The only data available for electron damage for this behavior in the high-dose regions are those due to Dworschak *et al.*[17] from their investigation of saturation effects upon damage rates. The value they report for the amount of stage-I recovery is much lower than the high dose values and shows this tendency toward decreasing recovery in stage I. This region, due to dimer formation by initial concentrations of defects, is region D. We are privileged to have access to some beautiful corroborative evidence for the behavior in region D in the form of unpublished results from the German group at Julich showing extensive results in copper over this range using α particles.[18] Although the curve in region D is lower for these particles as one might expect than for electrons, the decrease in stage I with increasing dose is unmistakable. Although there is a paucity of data points in this region for electron damage, the curve drawn is then not so arbitrary with the above results to guide us. Indeed, for the electron-damage case, one can estimate the point where the overlap effect begins. This point lies where the curve in region C begins decreasing into region D, and lies between 1 and 5×10^{-8} Ω cm which gives an upper limit to the interstitial interacion radius of $11a_0$ to $7a_0$ where a_0 is an fcc cube edge and $\Delta\rho_{\mathrm{F.P.}}=2.0\times10^{-4}$ Ω cm/unit concentration. This value for the upper limit of the interaction range of an interstitial in copper can be better pinned down when more high-concentration annealing data are available.

Presumably, the decrease in region D ends at some high defect concentration not definable from the present data. In this region E one might expect the curve to once again level off to a saturation value. This saturation value would be determined by the spontaneous recombination volume[17] for close Frenkel pairs and the relative ranges of interactions of the interstitials and vacancies which determine the relative numbers of dimer close pairs formed at irradiation to recoverable Frenkel close pairs. Of course, at such high doses the interstitial interactions would be such that higher complexes would also be formed. At present, though, this region remains mainly in the realm of speculation.

We recapitulate the interpretation of Fig. 7 in terms of damage remaining after the completion of stage I. In region A, where $i_0 \ll I_0$, I_E is completely suppressed with the remaining damage due entirely to impurity-trapped interstitials and their unrecovered vacancies, the interstitials being trapped during free migration. In region B where $i_0 \sim I_0$ vacancy-interstitial recovery begins to compete with impurity trapping during free migration with the damage remaining due to trapped interstitials, unrecovered vacancies, and some dimers beginning to be formed. In region C where $i_0 > I_0$ impurity-trapped contributions to damage remaining are negligible and unrecovered damage is attributed to dimer formation during free migration and unrecovered vacancies. In region D the concentration of interstitials reaches the point where overlap begins creating an increasing concentration of dimer close pairs, thereby decreasing the number of free interstitials available to annihilate vacancies in I_E. Thus in D the concentration of dimers increases as does the concentration of unrecovered vacancies at the conclusion of stage I. The

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[18] W. Schilling (private communication).

dimer concentration is due to dimer close pairs formed at irradiation and to dimer formation due to migrating single interstitials. Region E carries the D processes to extremes with each defect created during irradiation within the range of interaction of a previously created interstitial or vacancy (or combinations of the two) causing all defects to form either close Frenkel pairs or close dimer pairs that form interstitial agglomerates during stage-I annealing. The dimer concentration formed during free migration goes to zero as there are no unpaired interstitials available to migrate freely.

The variation of the kinetics of I_E can be followed schematically in Fig. 7 which reflects the concentration of unrecovered vacancies present. The present data show the kinetics to start at 1 in region A, increase through region B and approach a steady value between 1.6 and 1.8 in region C. Carrying this analysis further beyond the scope of presently available kinetics data, we expect the I_E kinetics to begin decreasing with increasing dose at the end of region C, decrease throughout region D to a final value of 1 at the beginning of region E. The assignment of a value of recovery kinetics to I_E for the saturation regions of E and also A may be without meaning since the recovery associated with I_E in these regions vanishes.

The comparison of copper recovery to that of silver has been successfully shown[19] and we feel that the above analysis involving Fig. 7 will also carry over and apply to silver as it does to copper.[16]

An alternative explanation to interstitial agglomerate formation would be to try to account for all the remaining damage through the impurity trap mechanism. In order to do this, first the demand is placed upon the traps that they be unsaturable. This demand is reasonable and is shown by Neely and Sosin[20] to possibly account for the 80°K production results in copper and aluminum. To account for the lack of dose dependence of the damage remaining at the end of stage I above low damage concentrations the effectiveness of the trapping sites would have to increase with increasing dose. However, this means that the traps are more efficient if they already contain trapped interstitials. Such behavior is discussed in the above paper[10] but no evidence for it is found. We prefer the former interpretation though the latter one is not completely ruled out.

Under this interpretation a more definite identification of the II_a substage shown in Fig. 5 can be made. It was pointed out earlier that the amount of recovery due to this substage was strongly dose-dependent, with the higher relative recovery for a lower dose. This is the behavior expected for a trap-release process and just opposite to that for interstitial cluster breakup, since clustering is more probable for the high dose than the low. Thus the identification, not surprisingly,[13] of II_a as a detrapping substage is made. The data are not extensive enough to distinguish as to whether the trap is of a saturable or unsaturable variety. Di-interstitial breakup for this substage is ruled out.

An estimate of the residual impurity concentration using the resistivity at helium temperature gave a value of about 2×10^{-5} concentration which is in reasonable agreement with the nominal stated purity of the sample material. On the basis of the analysis used here and the shape of the curve in Fig. 6 the estimate of I_0, the effective impurity-trap concentration, using $\rho_{\mathrm{F.P.}}=2\times10^{-4}$ Ω/cm unit concentration is $I_0=3\times10^{-7}$. Since the slope of the part of the curve in Fig. 6 is large in the region where the estimate is made, the error in defect concentration obtained due to differing points on the curve is small. Thus, it is deemed that the discrepancy between the values for the impurity concentrations and the effective trapping impurity concentration is a real effect and not due to error. The latter value obtained for I_0 is considerably smaller than the former value of 2×10^{-5}. An error of more than a factor of ten in the resistivity per Frenkel pair to account for the discrepancy also seems excessive, although theoretical calculations along this line do not rule it out.

A more reasonable explanation lies in assigning differing trapping efficiencies to the various species of impurities present. Many previous experiments on doping with dilute impurities have shown that different dopants have different effects on the suppression of stage I due to trapping.[2] Thus some impurity atoms are less effective as interstitial trapping centers than others. From the standpoint of total traps then, a lower concentration of impurities will be obtained than was obtained in the resistivity estimate where each impurity was presumably effective. Due to the influence of impurity trapping in 99.999% pure copper upon the production rate at 80°K, Neely and Sosin[20] have estimated I_0 from data fits. Their value was $I_0=1.3\times10^{-7}$. This value is also considerably less than the nominal value for 99.999% purity and is close enough to our value of 3×10^{-7} to be deemed in good agreement with it. Since the value that Neely and Sosin used for $\rho_{\mathrm{F.P.}}$ was 3×10^{-4} while the value we used was 2×10^{-4}, a discrepancy between results is expected. Had they used the value that we did, even closer agreement between the values of I_0 obtained would have been achieved.

VI. RECOVERY MODELS

We will not attempt here a review of all the recovery models put forward to account for point defect recovery but rather touch on those aspects which have a bearing on the present results and vice versa. Our results are in general agreement with the model put forward by Corbett[2] to explain recovery in copper, with some changes and extensions. Close Frenkel pair recovery through substage I_c is generally agreed upon.

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[19] F. W. Wiffen, C. L. Snead, Jr., and J. W. Kauffman, Phys. Letters 23, 22 (1966).

[20] H. H. Neely and A. Sosin, Phys. Rev. 152, 623 (1966).

The nature and complexity found in the low-temperature recovery spectra directly reflect the physical processes which occur in this range. The number and distribution of Frenkel pairs is a question of fundamental importance to the final understanding of recovery behavior. With the reporting of fine structure in the I_D region[3–7] and in the I_E region[3,6] a reinterpretation of the annealing processes active there appeared necessary. It was shown[3] that the additional structure found in I_D made the simple Waite theory[21] as applied by Corbett *et al.*[8] insufficient to explain I_D recovery. Although the observation of substructure within I_D does not eliminate a correlated recovery process, the apparent first order structure at least forces an extension of the Waite theory to include them. These first-order processes occur simultaneously with the correlated recovery. The possibility might be expected on the basis of Johnson's calculations[22] showing mutually trapped interstitials and vacancies possessing activation energies higher than that of correlated and free migration recovery.

High resolution of measurement, small temperature steps (no greater than 0.75°K), good temperature control, and careful approach to the annealing temperature are necessary factors in defining the substructure. Even then only a few data points define a peak lending little significance to peak shapes and widths. The character and indeterminability of the number of these peaks has been discussed.[23,24] In the present work, deviations in annealing time at temperature (albeit extreme to account for all the structure) could explain some of the smaller deviations. However, the structure on the I_D peak is deemed significant and well established, if not reproduced point by point, by different workers in several different laboratories.

Because of the additional structure reported in the I_E region,[3,6] von Jan[1] concluded that all the processes occurring there were first order and that the dose dependence exhibited was due to the selective shifts in peak heights rather than a shift of the center temperature of a I_E high-order peak. This interpretation differed from that of the reporting authors[3,6] for this region although they did apply it to the I_D recovery. Their interpretation for the I_E region was that there were several first-order peaks superimposed over a broad, higher-order peak corresponding to the free migration I_E substage. In the model of von Jan then there was no free migration substage present in stage I and recovery was due entirely to close pairs, leaving free migration to stage III.

In the results presented here there is structure found in the I_D region up to a temperature of about 47°K. This structure superimposes the I_E peak over a large portion of the peak in the high-dose case (see inset of Fig. 2) but is evidenced only on the lower part of the low-temperature side of the low-dose I_E curve. The I_E peak in the low dose is considered sufficiently separated from the substructure present and shifting in dose properly to be identified as a single, higher-than-first-order peak attributable to free interstitial migration. This is incompatible with the model proposed by von Jan.

For low doses the damage remaining after I_E will be impurity dominated and for high doses will be accounted for mostly by di-interstitial formation. Careful recovery studies above stage I for varying doses are necessary to test this contention. Recent recovery studies in this region by the North American group[25,26] for irradiations performed both at 4.2 and 70°K are interpreted in terms of the "conversion-two-interstitial" model. In this model the damage remaining at the end of stage I is due to the conversion of some of the crowdions which migrate in I_E to dumbbells, or normal interstitials, which migrate in stage III. If true, this mechanism replaces the di-interstitial formation process above for the higher doses but will be additional to the impurity dominated behavior in the low-dose case. Further work in these higher temperature regions is needed for clarification of these points and their corresponding implications for stage-I recovery.

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[21] T. R. Waite, Phys. Rev. **107**, 463 (1957); **107**, 471 (1957).

[22] R. A. Johnson, Phys. Rev. **145**, 423 (1966).

[23] G. W. Iseler, Ph.D. thesis, Northwestern University, 1966 (unpublished).

[24] H. I. Dawson and J. W. Kauffman, Phys. Letters **21**, 488 (1966).

[25] W. Bauer and A. Sosin, Phys. Letters **24**, A193 (1967).

[26] W. Bauer, A. Seeger, and A. Sosin, Phys. Rev. Letters **24**, A195 (1967).