Electron Irradiation of Copper and Aluminum above Stage I*

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The dependence of the increase of electrical resistivity upon integrated electron flux φ has been investigated in copper and aluminum. Irradiations were performed at 80°K using 1.1-MeV electrons. The resistivity was found to increase nonlinearly with φ up to the highest fluxes used: 10^{19} electrons/cm^2. At high φ values, the increase in resistivity appears to be proportional to $\varphi^{1/2}$. This dependence is predicted in a model in which interstitials, created during irradiation, are primarily annihilated by recombination with vacancies created concurrently during irradiation, but may alternatively be trapped by intrinsic defects such as impurities or dislocations.

I. INTRODUCTION

SEVERAL years ago, Coabett, Smith, and Walker[1] carried out an intensive investigation of the recovery of electrical resistivity upon heating below 60°K (stage I) following electron irradiation of copper near 4°K. Based on their results, it was generally accepted that, in copper, an interstitial-type defect migrates through the lattice in an essentially random fashion in the latter part of stage I. (The earlier portions of stage I were attributed to recombinations of close pairs—interstitials and vacancies located sufficiently close that direct pair recombination is inevitable upon thermal activation.) These results gave rise to what has come to be known as the stage III dilemma. Stage III represents the recovery stage in the near–room temperature region common to most metals. The dilemma arises since related experiments apparently rule against assigning stage III to vacancy migration, based on the observed value of the activation energy. In addition, electron irradiation, at the energies generally used, appears to result *directly* in no significant concentration of other defects beyond single interstitials and single vacancies.

These investigations were largely or wholly concerned with the recovery of electrical resistivity following irradiation at temperatures sufficiently low so that no defect mobility occurred during irradiation. Indeed, most radiation-damage studies are currently of this type. However, there is a different approach which may be pursued and the present investigation is of this variety. In this approach, the damage rate (the rate of introduction of defects as a function of integrated electron flux φ) is measured. The key consideration in such experiments is the temperature of irradiation. Performed at very low temperatures, these studies are important for the purpose of elucidating the defect-creation process. When performed at more elevated temperatures such that defect migration occurs during irradiation, the purpose of damage-rate experiments is more closely connected with recovery studies.

In principle, higher temperature damage-rate experiments may be divided into two classes. In the first class, the characteristic times which specify defect production and defect migration are comparable. The exacting experimental conditions which must be met in such experiments (e.g., precise temperature control, finely controlled beam currents) have generally ruled against this class in favor of the second class in which defect migration is sufficiently rapid that one may assume that the concentration of moving defects is essentially zero at any time.

In the case of most metals, a particularly convenient irradiation temperature for the latter class of damage-rate experiments is near liquid-nitrogen temperature. This temperature is easily accessible experimentally and is sufficiently well above stage I in temperature that the assumption of essentially instantaneous interstitial mobility is excellent. Numerous previous experiments have shown further that there are no further significant annealing stages in this temperature region. Accordingly, Walker[2] irradiated copper at 80°K and studied the damage rate. His results, carried to $\varphi=6.8\times10^{17}$ electrons/cm^2, differed from those reported earlier by Meechan and Brinkman,[3] carried to $\varphi=2.7\times10^{18}$ electrons/cm^2. One of the purposes of this study is to extend the 80°K damage-rate studies to higher fluxes than had previously been done in copper and in another metal—aluminum.

II. EXPERIMENTAL

Two irradiations were performed in this investigation. In the first, copper supplied by American Smelting

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[1] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. **114**, 1452 (1959).

[2] R. M. Walker, in *Radiation Damage in Solids*, edited by D. S. Billington (Academic Press Inc., New York, 1962), p. 594.

[3] C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

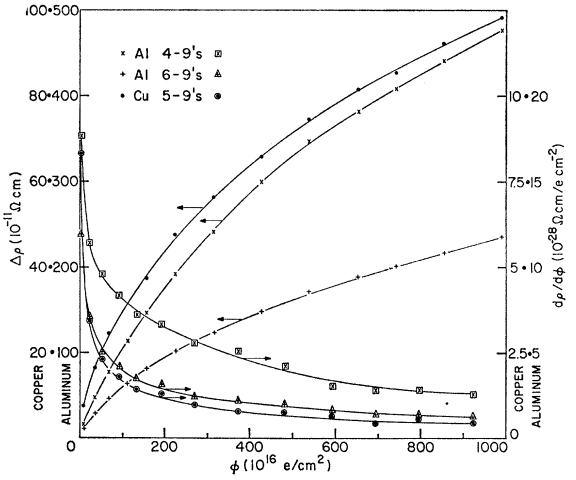

FIG. 1. Damage curves and differential damage curves for 1.1-MeV electron irradiation of copper and aluminum at 80°K.

and Refining Corporation (nominal purity 99.999%), aluminum supplied by Aluminum Corporation of America (nominal purity 99.995%; hereafter designated as 4-9's Al), and aluminum supplied by United Minerals Corporation (nominal purity 99.9999%; hereafter designated as 6-9's Al) were irradiated to 0.99×10^{19} electrons/cm^2. The pre-irradiation treatment consisted first of wire drawing down to final diameter 0.0053 cm. The wires were then mounted together on a single sample holder in a manner reported in earlier investigations.[4] Following mounting, the wires were heated to 450°C in a vacuum to anneal out the effects of sample preparation.

The electrical resistivities at 20.4°K prior to irradiation were as follows: Cu, $\rho_0=3.71$; 4-9's Al, $\rho_0=6.97$; 6-9's Al, $\rho_0=4.09$; all in units of 10^{-9} Ω cm. These values of ρ_0 include an appreciable temperature-dependent normal lattice scattering contribution in addition to the effects of residual impurities and dislocations and of surface scattering. A better estimate of the impurity content is offered in other experimental investigations we have carried out on these materials.[5] There it was observed that the residual resistivity (i.e., measurement at 4.2°K) of 4-9's Al materials were found to differ by a factor of approximately 4 and that the residual resistivity of 6-9's Al material is about 1×10^{-9} Ω cm. We believe, therefore, that the differences in over-all impurity levels in the two Al samples is of the order of a factor of 4.

The first irradiation was performed at 1.1-MeV incident electron energy. A second irradiation to a considerably lower exposure (2.02×10^{18} electrons/cm^2) was performed at 1.4 MeV on the Cu and 4-9's Al samples. No differences were observed between these experiments which would not be expected considering the differing energy of irradiation.

[4] A. Sosin and H. H. Neely, Phys. Rev. **127**, 1465 (1962).
[5] K. R. Garr and A. Sosin (to be published).

The experimental details of irradiation were similar to those reported previously for irradiation at 4.2°K or 20.4°K.[4] In this case, however, irradiations were performed at approximately 80°K. To obtain this temperature, the samples were isolated from direct contact with the reservoir filled with liquid hydrogen, using a mechanical valving and heater arrangement previously described. Measurements were made periodically at 20.4°K by opening the valve and shutting off the heater. In this way, irradiations were performed in vacuo, with no foil intervening between the electron source and the samples. This contrasts with the investigations of Meechan and Brinkman in which (in a completely different apparatus described elsewhere[3]) two foils intervened and temperature control depended on a flowing liquid-nitrogen technique. The techniques used here should have resulted in better electron energy control and current monitoring.

III. RESULTS

Figure 1 presents the primary results of this study. "Damage curves" (resistivity increase $\Delta\rho$ versus integrated electron flux φ) and "differential damage curves" (resistivity increase per unit electron flux $\Delta\rho/\Delta\varphi$ versus integrated electron flux φ) are plotted. No clear linearity between $\Delta\rho$ and φ is established by the former curves. In particular, the linearity reported by Meechan and Brinkman between 100 and 300×10^{16} electrons/cm^2 does not appear in these data. Furthermore, the latter curves show a continual decrease of $\Delta\rho/\Delta\varphi$ as a function of φ, within experimental error. These data fail to demonstrate conclusively whether $\Delta\rho/\Delta\varphi$ tends asymptotically toward zero at high φ or to some value, $(d\rho/d\varphi)_\infty$, above zero. The following upper limits may be established for $(d\rho/d\varphi)_\infty$: Cu, 0.5; 4-9's Al, 2.5; 6-9's Al, 1.2; each in units of 10^{-28} Ω cm per electron/cm^2.

In order to investigate the quantity $(d\rho/d\varphi)_\infty$ further, as well as to attempt to establish a functional dependence of $\Delta\rho$ on φ, particulary at high φ, the data are replotted in Fig. 2 on a ln $\Delta\rho$ versus lnφ basis. No saturation effect is established in this figure. Instead, the curves appear to be tending toward a constant (nonzero) slope; that is, $\Delta\rho=\mathrm{K}(\varphi)^n$ may be implied. Further, $n\approx\frac{1}{2}$. To test this dependence further, Fig. 3 is a plot of $\Delta\rho$ versus $\varphi^{1/2}$. The solid curves represent theoretical fits based on a model discussed below.

There is some indication in Fig. 2 that n may tend to decrease slowly to below $\frac{1}{2}$. This slow decrease is, we believe, due to an effect which is rather secondary to our interests here. This "saturation" effect has recently been examined by Dworschak *et al.*[6] They showed that the rate of increase of resistivity per unit electron flux in copper is not constant at fixed electron energy even

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

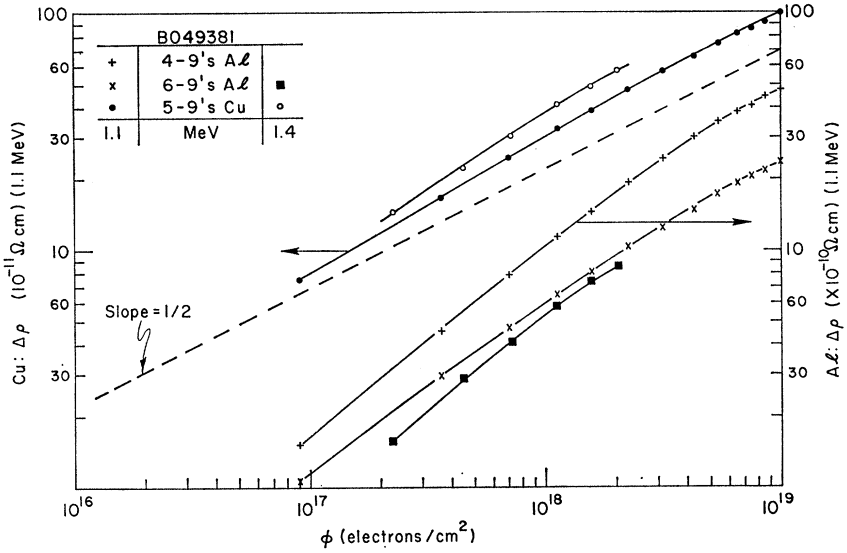

FIG. 2. Log-log plots of the damage curves of Fig. 1. Data pertaining to an additional experiment performed at 1.4-MeV electron energy are included for comparison. The ordinate in these latter plots has been adjusted for ease of comparison.

below 7.5°K. This decrease in rate is evidently due to the spontaneous recombination of Frenkel pairs, the recombination occurring when the spontaneous recombination volumes of two adjacent pairs accidentally overlap. Such accidental overlaps occur infrequently so that they were able to study saturation behavior only after extensive irradiation. For comparison, their total resistivity increase was 2.8×10^{-7} Ω cm (after an irradiation to 3×10^{19} electrons/cm² at 3 MeV). In the present experiment, the increase was 1.0×10^{-9} Ω cm. Even on correction for annealing below 80°K, the damage level in the present experiment is approximately thirty times smaller than achieved by Dworschak *et al.* We are led to believe, therefore, that $n=\frac{1}{2}$ is indeed the high flux dependence in the absence of saturation effects, but that saturation effects may be slightly resolvable in the present experiment.

IV. DISCUSSION

The results of this experiment may be fully appreciated only on consideration of a large amount of experimental and, to a lesser extent, theoretical evidance. In the interest of brevity, we shall largely restrict this discussion to an evaluation of how the present data testify for or against the various recovery models which are proposed to account for defect identification. This evaluation is specifically presented in the second portion of the discussion. In the first portion we discuss analytical models composed to explain the damage rate in the present experiment. The analytical models have, of course, been formulated with due regard to the recovery models discussed in the second portion.

A. Damage-Rate Models

1. One-Interstitial Models

We first consider a model in which an interstitial, created by irradiation, migrates rapidly either to a vacancy or to an "unsaturable trap." The analysis, as given by Walker,[2] centers about the equation

$$\frac{di_u}{d\varphi}=\sigma_d\frac{N_u}{N_u+v}, \tag{1}$$

where i_u is the concentration of interstitials trapped by

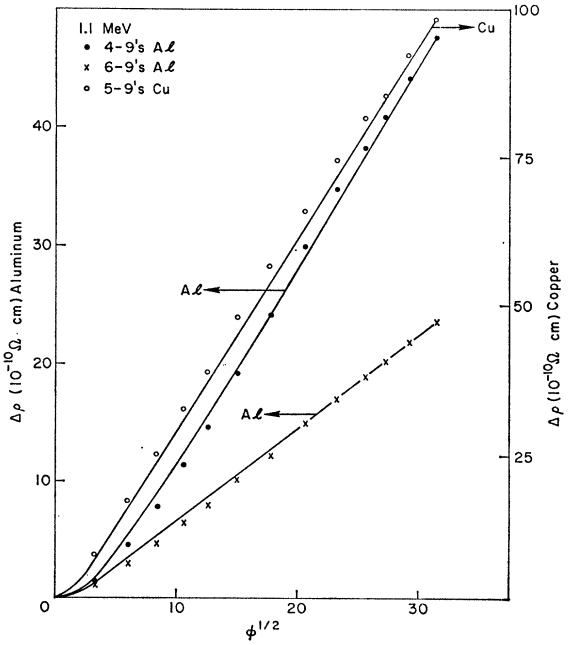

FIG. 3. A test of the $\frac{1}{2}$-power dependence on flux of the resistivity increase. The ordinate, flux to the $\frac{1}{2}$ power, is in units of $(10^{16}$ electrons $\mathrm{cm}^{-2})^{1/2}$.

TABLE I. Frenkel resistivity, concentration of traps, and atomic displacement cross sections used in the fit of an unsaturable trapping model.

	4-9's Al	6-9's Al	5-9's Cu
ρ_F	$5\times10^{-4}\,\Omega$ cm/(unit concentration)		$3\times10^{-4}\,\Omega$ cm/(unit concentration)
N_u	1.28×10^{-6}	0.28×10^{-6}	0.13×10^{-6}
σ_d	4×10^{-24} cm^2		4×10^{-24} cm^2

an unsaturable trap, N_u is the concentration of unsaturable traps, v is the concentration of vacancies, σ_d is the cross section for atomic displacement and φ is the integrated electron flux.

The resistivity increase, $\Delta\rho$ is

$$\Delta\rho=\rho_F(i_u+v)\,, \tag{2}$$

where ρ_F is the specific resistivity of vacancy-interstitial pairs.

Integrating Eq. (1), recognizing $i_u=v$, yields,

$$\Delta\rho=\rho_F N_u\left\{\left(\frac{2\sigma_d\varphi}{N_u}+1\right)^{1/2}-1\right\}. \tag{3}$$

At large fluxes, Eq. (3) displays a $\varphi^{1/2}$ dependence. This same dependence at large fluxes has been derived by Dienes and Damask[7] in a somewhat different manner. Best fits to Eq. (3) have been achieved with the parameters given in Table I.

We have also sought to fit the data to a model in which the traps are saturable

$$\frac{di_s}{d\varphi}=\sigma_d\frac{N_s(0)-i_s}{N_s(0)-i_s+v}=\sigma_d\frac{N_s(0)-i_s}{N_s(0)}, \tag{4}$$

where i_s is the concentration of interstitials trapped at saturable traps and $N_s(0)$ is the concentration of saturable traps.

Integrating Eq. (4) yields

$$i_s=N_s(0)\left\{1-\exp\left(-\frac{\sigma_d\varphi}{N_s(0)}\right)\right\}. \tag{5}$$

No satisfactory fit was obtained.

In formulating these models, it is appropriate to inquire as to the nature of the traps implicit in the model. It is tempting to identify dislocation sites with unsaturable traps. This identification is beset with certain difficulties, however. First, a value of $N_u\approx10^{-6}$ implies a dislocation density of about 10^9 cm^{-2}, which seems excessive. Secondly, the differing value of N_u in 4-9's and 6-9's Al by a factor of 4 is not easily explainable, although somewhat higher dislocation concentrations may be found in less pure metals.

On the other hand, $N_u\approx10^{-6}$ may be simply related to the density of impurities. To make this identification, we must conclude that impurities act as unsaturable trapping centers. We may lend credance to this conclusion on the basis of previous studies[4] involving trapping of copper interstitials by small concentrations of solute gold atoms. We showed then that there exist roughly 70 interstitial sites about a gold atom in which a single atom, upon reaching such a site in its diffusion, would be trapped. The implied trapping radius is sufficiently large that we are now led to suspect that the trapping potential of a single impurity atom for several interstitials may be considerable.

Walker has also discussed a model similar to this. In his formulation he allowed for an increase in the trapping effectiveness with increasing number of trapped interstitials at each nucleation site, in Walker's terminology. The importance of the increasing effectiveness was measured by a parameter $\gamma\leq1$. At high doses, the damage curve would become linear: $\Delta\rho\propto\varphi^1$. Since no evidence for this behavior is discernible in the present experiment, we conclude that $\gamma\approx0$.

The model suggested here may not be strictly an unsaturable-trap model; however, it is closer to that than a model based on saturable traps. Any attempt to develop an analysis for the characteristics of multiparticle traps does not appear warranted in the light of the satisfactory fit to the unsaturable-trap model, due, presumably, to the large trapping volume about impurities.

2. *Close-Pair Models*

The models explored above may be termed "second-order" models. By this we note that v appears in the denominators of the differential equations and the concentration of trapped interstitials was assumed to be equal to the vacancy concentration. The situation is different for close pairs. The unsaturable-trap model for close pairs is specified by the equation

$$di_u/d\varphi=\sigma_d N_u\,, \tag{6}$$

which integrates to

$$i_u=\sigma_d N_u\varphi\,, \tag{7}$$

a linear damage dependence. The saturable-trap model for close pair is specified by the equation

$$di_s/d\varphi=\sigma_d[N_s(0)-i] \tag{8}$$

which integrates to

$$i_s=N_s(0)\{1-\exp[-\sigma_d\varphi]\} \tag{9}$$

a saturating dependence parallel to Eq. (5). Neither of these dependences agrees with observation.

Consider the absence of a linear damage dependence (except, perhaps, at very high flux) and its implications

[7] G. J. Dienes and A. C. Damask, Phys. Rev. 128, 2542 (1962).

regarding close pair recombination. In our previous study,[4] we also explored the amount of suppression imposed by varying concentration of gold atoms in the region below 35°K where close pairs are known to recombine. At low impurity concentrations, the fractional suppression of recovery in this region was roughly 160; that is, an impurity content of 10^{-5} would retain about 1.6×10^{-3} of the close pairs below 35°K. The recovery below 35°K accounts for about 30% of the total damage injected at 4°K so that this fractional contribution to a permanent damage (persisting to higher temperatures) would be about 5×10^{-4}. In the remainder of stage I (i.e., between 35°K and about 55°K), the retention is even more effective by more than an order of magnitude and the percentage recovery is approximately twice the previous amount. Therefore, the fractional contribution to permanent damage due to trapping of interstitials which are members of close pairs in 5-9's copper may be 10^{-3} of the injected number. At 1.1 MeV and at 4°K, the damage rate is about 6×10^{-27} Ωcm/(electron/cm^2). Thus the permanent damage rate—a linear term in our model—due to such close-pair trapping would be roughly 0.06×10^{-28} in copper. Referring to Fig. 1, it is clear that such a possibility is not precluded; however, from Fig. 2 we see that fluxes between 10^{21} and 10^{22} electrons/cm^2 would be necessary to test this. The case is similar in both aluminum samples, presumably, but a linear effect of this variety may be expected to set in at lower fluxes in the sample with higher impurity content.

3. *Two-Interstitial Models*

In addition to considering models in which a single type of interstitial is created and then annihilated or trapped, we have examined models in which a second interstitial is created as well, but which possesses essentially no mobility. As one example, we have considered a revision of Eq. (1) in which the term on the right-hand side is multiplied by a fraction f and a second term is added: $(1-f)i_2$. Here, i_2 is the concentration of the second type of interstitial. No such model appears to account for the data. The difficulty arises from the simple fact that, at sufficiently high integrated flux, a linear damage curve must result. This is the case whether saturable or unsaturable traps are effective in preserving the more mobile species of interstitial. No such linear region has been established even at the highest fluxes used. Any tendency to develop a linear damage curve, if it does occur, must take place at much higher flux—say 10^{20} or 10^{21}—and, concommitantly, involve a small number of second type of interstitials. (On the basis of Fig. 1, one might speculate on such a linear region in 6-9's Al over the last half of the damage curve. Figure 2 does not appear to support this. In any case, full linearity would be established only at higher fluxes, in accord with these remarks.)

B. Point-Defect Recovery Models

In relating the present data to recovery models, we first emphasize that the discussion of the previous section appears to demonstrate that an appreciable amount of interstitial diffusion occurs during irradiation at 80°K in Cu and Al. Mere close-pair annihilation cannot account for the observed flux dependences. A second apparently direct conclusion which can be drawn is that no significant concentration of dimers (two self-trapped interstitials) are generated during irradiation at 80°K since the probability of two interstitials encountering one another during irradiation is completely negligible (the instantaneous concentration of single free interstitials during 80°K irradiation is slight). It does not follow from this conclusion concerning the absence of dimers in 80°K irradiation that dimers are not a significant product in experiments involving irradiation at 4°K followed by heating to 80°K. However, it has been amply demonstrated that stage III is a significant recovery stage following 80°K irradiation in both Cu and Al.[3,8] The absence of dimers in 80°K irradiation does, nevertheless, imply that stage III cannot be ascribed solely to the migration or dissociation of simple dimers.

Accordingly, the principal conclusion which appears to follow from this experiment is that the defects which are preserved during radiation at 80°K consist of trapped interstitials, which have previously migrated to bound positions, and isolated vacancies. No appreciable concentration of "second-type interstitials," which have not migrated appear to be consistent with the data. This must certainly be viewed, as a serious argument against the two-interstitial model—a model which we have generally favored for some time. We have been able to find only one mechanism to preserve the two-interstitial model, a mechanism recently suggested by Dworschak and Koehler.[9] They suggested that the interstitial which moves in stage I might be converted into a second type of interstitial which moves in stage III. In suggesting this mechanism, they specifically noted that the strain fields near one interstitial might aid in the conversion of the other. While such a mechanism is not ruled out in the present experiment, it cannot in itself explain the results since the concentration of free interstitials is negligible, as pointed out earlier. However, the mechanism is preserved by assuming that impurity atoms perform the function of converting interstitials from one type to to another. This mechanism is appealing in that the impurity concentration plays a significant role, as indicated in the present work. However, until the actual details of such a conversion are examined, such a mechanism must be viewed as merely speculative.

The simplest model consistent with the present data would ascribe stage III to migration of vacancies to

[8] A. Sosin and L. H. Rachal, Phys. Rev. **130**, 2238 (1963).
[9] F. Dworschak and J. S. Koehler, Phys. Rev. **140**, A941 (1965).

interstitials which have been trapped previously. The principal argument against this vacancy model is one of long standing. It is that the activation energy measured in stage III is significantly lower than the migration energy for vacancies which may be derived by subtracting the formation energy of vacancies from the self-diffusion energy. This objection is particularly strong in the case of Cu; there is still controversy in the case of Al. Only an extended discussion, beyond the scope of this section, can adequately treat this matter.

For completeness we note further that the assignment of the migration of divacancies to stage III encounters sufficient difficulties that we cannot accept such a divacancy model as adequate for an understanding of stage III.

How then are we to interpret these results with regard to the stage III dilemma? The simplest interpretation appears to be one in which interstitials are freed from particularly deep traps and migrate to an equal concentration of vacancies. The difficulties with this suggestion arise from the identification of the trap and from appreciating how a concentration of about 10^{-5} to 10^{-6} of such traps can bind interstitials whose concentration may reach 10^{-3} (in the experiments of Burger *et al.*[10]) with no apparent saturation of trapping effectiveness. With respect to the identification of the traps, none of a series of elements explored as candidates for impurity traps to date seem to qualify—to enhance the size of stage III significantly with increasing impurity concentration. But it is only fair to note that the number of impurities which have been studied is appreciably less than those that remain as possible candidates. For example, the role of oxygen is still not known.

With respect to the high dose work of Burger *et al.*, we can only emphasize that the data presented in this paper are interpreted in terms of unsaturable traps. Whether dislocations or impurities act as traps, a 10^{-3} concentration of trapped interstitials would give rise to interstitial clusters, for which there is some experimental evidence as well.[11] The relative constancy of the activation energy for stage III would indicate that the trapping of an interstitial by an impurity is not significantly effected by previous trapping of other interstitials. Furthermore, the second-order kinetics reported for stage III would also be consistent with this model. This may be demonstrated as follows. Consider the reactions

$$v+i_f \xrightarrow{K_1} 0,$$

$$i_f+I \underset{K_3}{\overset{K_2}{\rightleftarrows}} i_t+I,$$

where i_f is the concentration of free interstitials, i_t is the concentration of trapped interstitials, I is the impurity (trapping) concentration (assumed constant), and the K's are the rate constants for the reactions. These expressions lead to the equations

$$dv/dt=-K_1vi_f, \tag{10}$$

$$di_f/dt=-K_1vi_f-K_2i_fI+K_3i_t. \tag{11}$$

In the stage-III region we may take $di_f/dt\cong 0$; in fact, i_f is always close to zero. As a consequence, $v\cong i_t$. From Eq. (11),

$$i_f\cong\frac{K_3i_t}{K_1v+K_2I}\cong K_3v/K_2I, \tag{12}$$

where we have assumed that $K_1v\ll K_2I$. Inserting this into Eq. (10),

$$dv/dt\cong-(K_1K_3/K_2I)v^2. \tag{13}$$

V. SUMMARY

In this paper we have shown that in the cases of copper and aluminum of relatively high purity, the electrical resistivity increase due to electron irradiation at 80°K proceeds in a nonlinear manner (except, possibly, at the very highest fluxes) up to 10^{19}electrons/cm^2. The shapes of the resistivity-versus-flux curves have been discussed, based on several models. A model in which interstitials are primarily annihilated at vacancies or trapped by unsaturable traps has been found to give a reasonable fit to the data. The identity of the unsaturable trap is not firmly established. Both dislocations and impurity atoms have been examined as candidates for the trapping centers. The identification with impurity atoms appears to be more satisfactory.

We have also shown that the model is consistent with some of the major features of stage-III recovery. These considerations do not prove the validity of the model but are sufficiently convincing that more exhaustive analysis of the model is clearly appropriate.

ACKNOWLEDGMENTS

We would like to acknowledge valuable discussions with W. Bauer, J. A. Brinkman, and D. O. Thompson.

[10] G. Burger, H. Meissner, and W. Schilling, Phys. Status Solidi 4, 267 (1964).

[11] M. J. Makin, A. D. Whapham, and F. J. Minter, Phil. Mag. 6, 465 (1961).