Thermally Activated Point Defect Migration in Copper*

C. J. MEECHAN, A. SOSIN, AND J. A. BRINKMAN
Atomics International, Canoga Park, California
(Received April 20, 1960; revised manuscript received June 6, 1960)

A recovery model is presented which includes specific assignments of point defect migration to the various recovery stages in copper. New experimental results showing the effects of prior cold work on the production and subsequent recovery of damage produced in copper by 10°K and 90°K electron irradiations are also presented. The most significant observations in these experiments are: (1) irradiation recovery Stages I_D and I_E are suppressed by previous cold work; (2) this suppression is reflected in an increased damage rate at 90°K; (3) the additional damage which remains in Stages I_D and I_E, or which is produced at 90°K, recovers in Stage III; (4) the recovery in Stage III is altered from the bi-molecular process characteristic of annealed copper; (5) under certain conditions a super-recovery occurs in Stage III so that the measured resistivity drops below the pre-irradiation value. These observations are interpreted according to this recovery model.

I. INTRODUCTION

In previous publications,[1,2] a model was presented to account for recovery of physical property changes in the noble metals following charged particle irradiation. Recently, data have been presented in the literature which cannot be explained by this model without some amplification and modification. In this paper a revised and expanded version of the previous model for copper is presented. Several aspects of the model are also applicable to gold.

In the following discussion, the recovery stages in copper and gold are referred to as Stages I, II, III, IV, and V.[3] Stage I in copper has been subdivided into I_A, I_B, I_C, I_D, and I_E.[4] The absolute temperature at which any recovery stage is "centered" depends upon the particular treatment given; therefore, when a particular recovery stage is defined in terms of a specified temperature range for electron irradiation recovery, this range may differ for the same recovery stage following other types of irradiation or other treatments. Nevertheless, the use of the recovery stage nomenclature has come into general use in the field, and is extremely useful in detailed discussions. As a general guide, we shall use the following temperature ranges for identifying the recovery stages in copper and gold, recognizing that some exceptions exist:

Stage I . . . 0°K to 60°K,

Stage II . . . 60° to 220°K,

Stage III . . . 220°K to 340°K,

Stage IV . . . 340°K to 450°K,

Stage V . . . above 450°K.

The modifications which are made to the previous model are based primarily on a consideration of four factors: (1) the demonstrations by Corbett, Smith, and Walker,[5] Cooper, Koehler, and Marx,[6] and Thompson, Blewitt, and Holmes,[7] that an interstitial-type defect becomes mobile in Stage I in irradiated copper; (2) the large amount of evidence for the assignment of single vacancy migration to Stage IV recovery; (3) the concepts that two distinct interstitial configurations may exist simultaneously in the copper lattice, and that conversion of one to the other is possible under appropriate conditions; and (4) the new experimental results presented in Secs. III and IV of this paper.

It has frequently been argued in the literature, primarily on the basis of factor (1), that interstitials migrate in Stage I and vacancies in Stage III in copper. It is our belief that consideration of both (1) and (2) requires the introduction of an additional defect to our model. The concepts mentioned in factor (3) arose in the discussions at a recent conference,[8] and we feel that they provide a satisfactory solution to the difficulties which ensue when an attempt is made to explain the existence of these three recovery stages with only two defects. Detailed arguments for our specific assignments are given in Sec. II. Sections III and IV describe a series of new experiments which were performed for the purpose of testing and gaining further evidence for these assignments. The results of these experiments are compatible with our model and, in addition, they provide new experimental information regarding a defect produced in copper by cold work which we believe to be the tri-vacancy.

II. FOUNDATION OF MODEL

We shall outline our revised recovery model, incorporating the more recent data in the appropriate places.

* This work was performed under contract with the U. S. Atomic Energy Commission.

[1] J. A. Brinkman, C. E. Dixon, and C. J. Meechan, Acta Met. **2**, 38 (1954).

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

[3] See, for example, A. Seeger, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin **7**, 557 (1955).

[4] J. W. Corbett and R. M. Walker, Phys. Rev. **110**, 767 (1958).

[5] J. W. Corbett, R. R. Smith, and R. M. Walker, Phys. Rev. **114**, 1452 (1959); **114**, 1460 (1959).

[6] H. G. Cooper, J. S. Koehler, and J. W. Marx, Phys. Rev. **97**, 599 (1955).

[7] D. Thompson, T. Blewitt, and D. Holmes, J. Appl. Phys. **28**, 742 (1957).

[8] A. Sosin, J. A. Brinkman, and C. J. Meechan, Phys. Today **12**, 30 (1959); Atomic Energy Commission Report NAA-SR-3250, 1960 (unpublished).

In a recent article,[8] a list was given of the various lattice imperfections which are thought to exist. Since at least nine distinct types of defects have been proposed, it seems imperative to make a definite assignment of the migration of at least one type (preferably one of the simpler ones, such as the isolated vacancy or interstitial) and proceed to build the model from this point. It is our belief that a specific assignment for the recovery stage resulting from single vacancy migration in copper and gold can be made with greater confidence than that resulting from migration of any of the other defects. The reasons for this belief are based on a variety of experimental and theoretical studies as well as a confidence in the existence of a single, distinct configuration for the vacancy, as opposed to the possible existence of two or more interstitial configurations. From this foundation, we shall proceed with the formulation of the model. Since it is generally agreed that vacancy migration occurs in either Stage III or Stage IV, we shall limit our arguments concerning this defect to these recovery regions.

A. Evidence Against Vacancy Migration in Stage III

Direct experimental evidence which supports the contention that Stage III is not the result of vacancy migration in copper is rather meager. A direct argument can be given, however, based on the results of theoretical calculations of the formation energy of vacancies, E_f, in copper. Separate calculations have been made in the past by Huntington,[9] Fumi,[10] Tewordt,[11] and Seeger and Mann,[12] all yielding values of E_f between 0.9 and 1.1 ev. The activation energy for recovery in Stage III following electron irradiation at 80°K is observed to be 0.60 ev.[2] This must be interpreted as the activation energy for migration of vacancies, E_m, if vacancy migration is assumed responsible for Stage III. Since self-diffusion in copper undoubtedly occurs by a vacancy mechanism, $E_d=E_m+E_f$, where E_d is the self-diffusion activation energy. The value of E_d is 2.1 ev,[13] a value some 0.4 to 0.6 ev greater than that predicted by the sum of the theoretical value for E_f and the 0.6-ev value for E_m which follows from the assumption that vacancy migration is responsible for Stage III. This discrepancy implies strongly that the assignment of the 0.6-ev activation energy to vacancy migration is incorrect. Conversely, if one rejects the theoretical values for the vacancy formation energy and insists upon the assignment of 0.6 ev to vacancy migration as an experimentally determined value, then one is forced to conclude that E_f must be about 1.5 ev. This in turn predicts a vacancy concentration just below the melting point approximately two orders of magnitude lower than the vacancy concentration near the melting point in gold.[14,15] A formation energy in agreement with the theoretical values, on the other hand, would give a vacancy concentration near the melting point in copper comparable with that in gold.

Direct experimental evidence is available, in the case of gold, indicating that Stage III does not result from vacancy migration. Both Stage III and Stage IV have been observed in gold following cold work.[16] Stage III does not appear to be a singly activated process in this case; however, Stage IV exhibits an activation energy of about 0.85 ev, in agreement with the value observed for migration of quenched-in vacancies.[14]

The above arguments imply quite strongly that Stage III recovery in both copper and gold is not a result of single vacancy migration.

B. Evidence for Vacancy Migration in Stage IV

(1) The first evidence presented for this assignment came from an analysis of the electrical resistivity recovery kinetics in cold-worked copper.[1] The kinetics were of the form expected for the diffusion of an initially random distribution of point defects to infinite sinks. From this analysis it was deduced that vacancies migrate in this temperature range with an activation energy of 1.19 ev.

(2) A radiation annealing experiment[17] was performed in which cold-worked copper was irradiated with electrons at temperatures between 313°K and 423°K. While the rate of thermal recovery (beam off) at temperatures between 373°K and 423°K was nearly zero, a substantial resistivity decrease occurred during bombardment in this temperature range. The temperature dependence of this recovery was studied and it was observed that the rate of recovery became negligibly small at and below approximately 363°K. It was concluded that one of the defects produced by electron bombardment attains appreciable mobility above 363°K. A theoretical analysis of the temperature dependence of this recovery yielded an activation energy in reasonable agreement with the value determined in the previous work,[1] interpreted as the activation energy for vacancy migration.

(3) Within the last year, elastic modulus measurements were made on electron irradiated copper.[18] A modulus increase was observed upon annealing in Stage IV. The direction of the effect is not consistent with the release of trapped defects from dislocations. The most direct interpretation is that vacancies migrate to and pin dislocations in Stage IV, in agreement with the conclusions reached in (1) and (2) above.

[9] H. B. Huntington, Phys. Rev. **61**, 325 (1942).
[10] F. G. Fumi, Phil. Mag. **46**, 1007 (1955).
[11] L. Tewordt, Phys. Rev. **109**, 61 (1958).
[12] A. Seeger and E. Mann, J. Phys. Chem. Solids **12**, 326 (1960).
[13] A. Kuper, H. Letaw, L. Slifkin, E. Sonder, and C. T. Tomizuka, Phys. Rev. **96**, 1224 (1954).
[14] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).
[15] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).
[16] W. Schule and A. Seeger (results quoted in reference 27).
[17] C. J. Meechan, J. Appl. Phys. **28**, 197 (1957).
[18] A. Sosin and L. L. Bievenune, J. Appl. Phys. **31**, 249 (1960).

(4) Some of the most conclusive evidence supporting the contention that vacancies migrate in Stage IV was recently obtained by Schule and Seeger.[16] They found that the Stage IV recovery in cold-worked gold exhibited an activation energy of 0.85 ev, in excellent agreement with the results of the gold quenching experiments[14] where E_m was observed to be 0.82 ev. Stage III recovery was also observed as a separate recovery stage in this same experiment. It is, therefore, extremely unlikely that the 0.82-ev activation energy in gold is to be ascribed to the same process as the 0.6-ev activation energy in copper.

(5) Additional evidence supporting the assignment of vacancy migration to Stage IV is found in the copper quenching experiments of Airoldi, Bacchela, and Germagnoli.[19] They observed a recovery near 650°K[20] and determined a value of E_m of (1.2 ± 0.1) ev, in good agreement with the earlier determinations.[1,17]

(6) Finally, one can appeal to a comparison of other materials with copper. Data have been compiled on Cu_3Au which demonstrate that vacancies migrate near 373°K[21] and that there also exists an additional recovery stage[1] corresponding in temperature to Stage III in which vacancy migration does not occur. Recent experimental results on defect recovery in nickel[22] show a remarkable similarity to copper, and here Stage IV has been investigated in considerable detail by measurements of hardness, density, stored energy release, resistivity, and lattice parameter.[23] It was concluded from these studies that Stage IV in nickel is a result of vacancy migration and annihilation.

All of the above results indicate strongly that both Stage III and Stage IV recovery are quite general in that they are both found not only in copper and gold but also in certain other fcc metals and alloys. Furthermore, we feel these results show conclusively that vacancy migration should be ascribed to Stage IV and not to Stage III.

C. Assignment of Interstitial Migration

Electrical resistivity recovery in Stages I and III in copper has been studied quite extensively following both electron irradiation[2,4,5] and deuteron irradiation.[6,24] Unique activation energies have been found in both recovery stages, and the kinetics of the recovery have been determined. In addition, the recovery of lattice parameter and length changes have been studied following deuteron irradiation.[25,26] From the latter results, the conclusion has been drawn[27] that most or all of the recovery in both Stages I and III following deuteron irradiation (and presumably following electron irradiation, too, since the activation energies agree) is the result of the direct annihilation of interstitials and vacancies. Since we have ascribed single vacancy migration to Stage IV, this annihilation must result from the occurrence of thermally-activated processes other than single vacancy migration, unless more than one kind of single vacancy exists in copper.

Corbett, Smith, and Walker[4,5] have shown quite conclusively that a point defect produced by electron irradiation is mobile in the copper lattice in Stages I_D and I_E (33°K to 48°K and 48°K to 65°K). In view of their arguments, as well as those given above, we are led to the conclusion that this defect is an interstitial-type defect. The question then arises as to what defect is migrating in Stage III. One can suggest at least six possibilities: (1) migration of di-interstitials (or higher multiples) formed when single interstitials encounter each other in their migration through the lattice: (2) migration of di-vacancies (or higher multiples) formed directly by the irradiation; (3) migration of a second kind of vacancy; (4) migration of a second kind of interstitial; (5) release of interstitials from traps; (6) break up of defect complexes or impurity-defect complexes.

The last two possibilities are eliminated by two observations: (1) Stage III recovery following electron irradiation accurately obeys the chemical rate equation with an order of 2.0, and (2) this stage is also characterized by a single unique activation energy. If the rate-limiting step were the release of Stage I-type interstitials from traps (as would be required to explain the 0.60-ev activation energy), then the kinetics should be first order rather than second. If several different types of traps are involved, then the total recovery would consist of several first order processes which might approximate a pure second-order reaction. In this case, however, the recovery would not be characterized by a single unique activation energy as is observed. Further doubt is cast on the contention that possibility (6) con-

[19] G. Airoldi, G. L. Bacchela, and E. Germagnoli, Phys. Rev. Letters **2**, 145 (1959).

[20] It is worth considering in this connection the dissimilarity between copper and gold insofar as Stage IV recovery is concerned. The activation energies are substantially different (0.82 ev for gold and 1.2 ev for copper) but the temperatures at which recovery is observed following quenching differ by even a larger factor (360°K for gold and 650–700°K for copper). The average number of jumps made by vacancies in quenched copper in migrating to a sink is therefore appreciably larger than in gold; Airoldi, Bacchela, and Germagnoli[19] estimate it to be 10^6 to 10^7. Since this is appreciably larger than the reciprocal of the quenched-in vacancy concentration, one can conclude that vacancy removal does not occur through divacancy formation, as it probably does in gold. Migration to dislocations is probably the annihilation mechanism for vacancies in copper, since this can account for the large difference in the temperature at which Stage IV is observed in quenched copper[19] (~675°K) and cold-worked copper [D. B. Bowen, R. R. Eggleston, and R. H. Kropschot, J. Appl. Phys. **23**, 630 (1952), and reference 1] (~400°K) as a result of the large difference in sink concentration.

[21] R. A. Dugdale, Phil. Mag. **1**, 537 (1956).

[22] A. Sosin and J. A. Brinkman, Acta Met. **7**, 478 (1959).

[23] L. M. Clarebrough, M. E. Hargreaves, and G. W. West, Phil. Mag. **1**, 528 (1956).

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

[25] R. O. Simmons and R. W. Balluffi, Phys. Rev. **109**, 1142 (1958).

[26] R. Vook and C. Wert, Phys. Rev. **109**, 1529 (1958).

[27] A. Seeger, *Proceedings of the Second United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958* (United Nations, Geneva, 1959), paper No. 998.

tributes appreciably by considering the new data presented later in this paper. It is demonstrated that the magnitude of Stage III recovery is enhanced at the expense of Stages I_D and I_E in cold-worked electron-irradiated copper. These observations, together with the fact that the second order kinetics are depressed towards unity following this treatment, are difficult to understand from the viewpoint of possibility (6).

Possibility (2) can be eliminated by considering the magnitude of the recovery in Stage III relative to that in Stage I. It is relatively easy to calculate an upper limit for the ratio of di-vacancies to single vacancies produced by electron irradiation of any given energy. This ratio should increase rapidly with increasing electron energy in the range from 1.0 to 1.5 Mev. The ratio of the amount of Stage III recovery to Stage I recovery which we find following 1.25-Mev electron irradiation is greater, not less, than the ratio found by Corbett *et al.* at 1.4 Mev. Furthermore, the magnitude of Stage III relative to Stage I obtained by Corbett *et al.* as well as that obtained in the present work, is at least a factor of two larger than one calculates, assuming di-vacancies to have twice the resistivity of singles. The observation of second-order kinetics in Stage III is also difficult to explain on the basis of possibility (2). The data presented later in this paper constitute a strong argument against possibility (1), since it is difficult to imagine how cold work can drastically increase the relative number of Stage I interstitials which become paired.

Only possibilities (3) and (4) remain, implying quite strongly that electron irradiation produces single point defects other than the Stage I interstitial and the Stage IV vacancy. At least three reasons exist for choosing possibility (4) over possibility (3). First, two distinct kinds of interstitial configurations have been suggested. Second, the second-order kinetics of Stage III should be obeyed for possibility (4), but is highly unlikely for possibility (3). Third, recovery Stages I_D and I_E are not observed following cold work at liquid helium temperature.[28] Since cold work is believed to produce at least one kind of interstitial,[27] and Stage III recovery is observed following cold work[29] (as well as Stage IV),[30] possibility (4) offers an explanation for this otherwise unexplained paradox.

The two kinds of interstitial configuration which we believe to be responsible for the recovery Stages I_D, I_E and III, are (1) the *C* configuration of Huntington[31] in which two atoms in a $\langle 100\rangle$ orientation are situated on opposite sides of a normal lattice site (hereafter referred to as the normal interstitial) and (2) a crowdion[32] aligned along a $\langle 110\rangle$ direction. Recent calculations by Vineyard, Gibson, Goland, and Milgram[33] indicate that both of these configurations can be produced by electron irradiation although the crowdion is not a stable or metastable static configuration in their model. Nevertheless, because of the need for a second kind of interstitial configuration developed in the above arguments, and because of the absence of any other postulated configurations, we will presume that both the normal interstitial and the crowdion can exist and undergo thermally activated migration as separate, distinct defects in the copper lattice. We assume the crowdion to be metastable, the energy barrier preventing its conversion to a normal interstitial being greater than its activation energy for migration.[34]

Having chosen two interstitial configurations, we must next assign the migration of one to Stages I_D and I_E and the other to Stage III recovery. We do this on the basis of the observation, mentioned earlier, that cold work produces a Stage III recovery but no Stage I_D and I_E recovery. It is expected that cold work will produce the normal interstitial in substantial numbers.[27] The production of crowdions by such treatment, however, is not at all obvious from geometrical considerations. It seems most reasonable, therefore, to conclude that crowdion migration is responsible for recovery Stages I_D and I_E and migration of the normal interstitial is responsible for Stage III recovery. It should be pointed out that this assignment differs from that of Corbett *et al.*, who ascribe migration of the normal interstitial to Stages I_D and I_E. They rejected the crowdion assignment on the contention that an excessive number of jumps, calculated in the manner prescribed by Lomer and Cottrell,[35] is required for a crowdion to reach a vacancy. However, they also point out that conclusions based on such jump arguments are rather unreliable and should not be considered definitive. The present experimental studies, described below, yield further evidence from which a conclusion can be drawn as to which interstitial is responsible for each of these recovery stages.

III. NEW EXPERIMENTS

Most of the studies of defect production and recovery which have appeared in the literature have been carried out on pure metals using one treatment such as particle

[28] C. J. Meechan and A. Sosin, J. Appl. Phys. **29**, 783 (1958).
[29] R. R. Eggleston, Acta Met. **1**, 679 (1953).
[30] D. B. Bowen, R. R. Eggleston, and R. H. Kropschot, J. Appl. Phys. **23**, 630 (1952).
[31] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).
[32] H. Paneth, Phys. Rev. **80**, 708 (1950).
[33] G. H. Vineyard, J. B. Gibson, A. N. Goland, and M. Milgram, Bull. Am. Phys. Soc. **5**, 26 (1960).
[34] Although relatively few data are available on the Stage I recovery of irradiated gold, it appears that a major difference exists in this recovery stage between copper and gold. Cooper, Koehler, and Marx[6] have observed little if any recovery of electrical resistivity in Stage I for gold following deuteron irradiation near 12°K, whereas approximately 50% of the induced damage recovers in this stage for copper following the same treatment. They further observed that Stage III is greater in gold than in copper, and that the total recovery up to and including Stage III is nearly identical for the two metals. These facts may be an indication that the static crowdion configuration is completely unstable in gold and therefore only the normal interstitial is observed to migrate. Obviously, more data are needed before a more definite statement can be made in this connection.
[35] W. M. Lomer and A. H. Cottrell, Phil. Mag. **46**, 711 (1955).

TABLE I. Schedule for cold-work and irradiation treatments.

Specimen	Pre-irradiation treatment: Area reduction (293°K)	Pre-irradiation treatment: Annealing schedule	$\rho_{4.2}$ (10^{-8} ohm cm)	Exposure (10^{18} e/cm²)	$\Delta\rho$ (10^{-9} ohm cm)
CW-1	16%	373°K for 30 min	1.013	3.6	2.778
CW-2	16%	293°K for 5 hr	1.046	3.7	2.695
CW-3	32%	373°K for 30 min	1.850	2.6	2.986
CW-3*a*	32%	373°K for 30 min	1.758	3.7	3.194
CW-4	32%	293°K for 5 hr	1.910	2.6	2.882
CW-5	92%	373°K for 30 min	2.927	2.6	2.956
CW-5*a*	92%	373°K for 30 min	3.027	2.5	3.225
CW-6	92%	293°K for 5 hr	3.242	2.6	2.832

ρ_0(annealed) $=3.4\times10^{-9}$ ohm-cm

irradiation, cold work or quenching from high temperatures. While these investigations have been extremely fruitful, we believe that a systematic investigation of the effects on damage production and subsequent recovery caused by such a combination treatment as irradiating specimens with varying dislocation densities should also prove helpful in arriving at a satisfactory model for radiation damage recovery.

Cold-worked specimens were prepared by drawing annealed copper wires of 99.999% purity through dies at approximately 300°K. For the 90°K irradiations, area reductions of 16%, 32%, and 92% were used and the final diameters were 0.014 inch in all cases. One set of specimens was then annealed at 293°K for five hours and another set at 373°K for 30 minutes. Resistivity measurements were made at 4.2°K using standard potentiometric methods with a measuring current of 4.3 amperes. The relative error in the resistivity measurements is approximately $\pm1\times10^{-12}$ ohm-cm. After the above treatment, irradiations were performed at 90°K with 1.25-Mev electrons. Table I lists the various treatments and resulting effects on the resistivity for each specimen. For the irradiations below 10°K, 29% and 91% area reductions were used and the final specimen diameters were all 0.0021 inch. Measurements were again made at 4.2°K with a measuring current of 0.4 ampere. The manner of irradiation and target box design will be described elsewhere. These samples were irradiated with 1.0-Mev electrons.

The exposure curves obtained at 90°K for all of the cold-worked specimens are shown in Fig. 1 along with

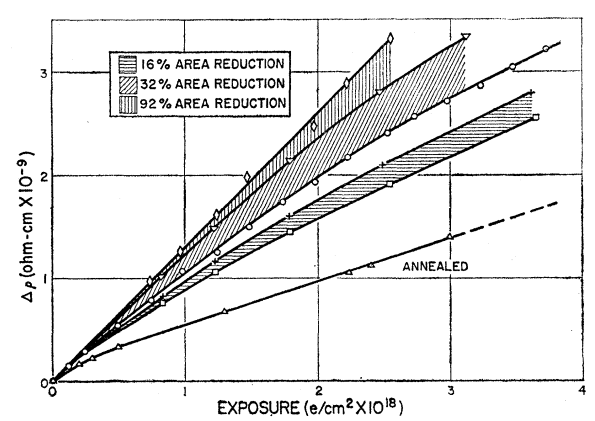

FIG. 1. Curves showing the effect of prior cold work on the 90°K exposure curves of copper for 1.25-Mev electron irradiation.

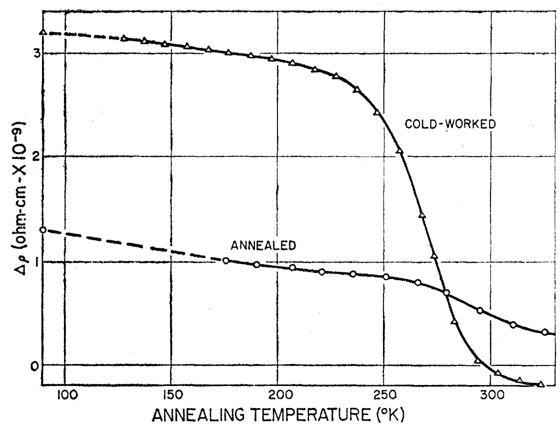

FIG. 2. Isochronal recovery of resistivity of cold-worked (*CW*-3*a*) and annealed (*A*-1) copper following 1.25-Mev electron irradiation at 90°K.

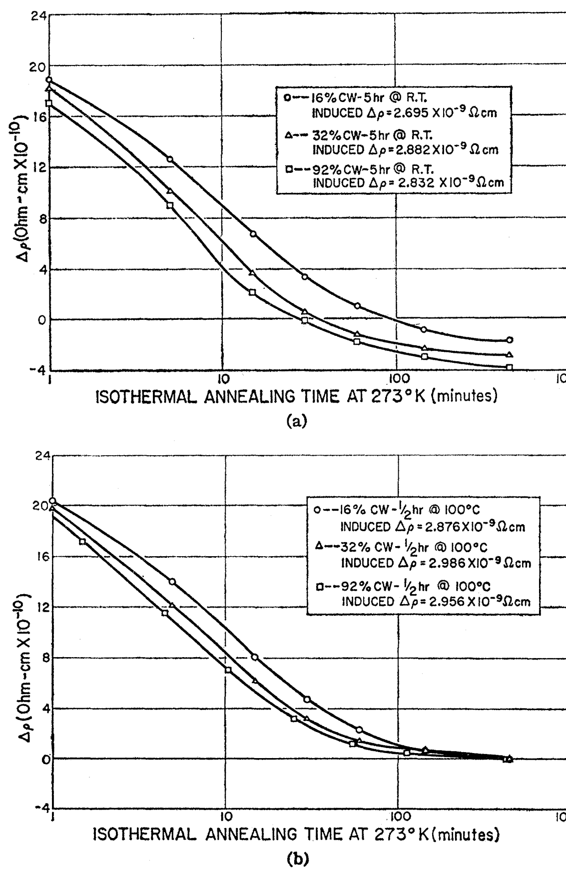

FIG. 3. (a) Isothermal recovery of resistivity of copper cold-worked and annealed at 293°K before irradiation. (b) Isothermal recovery of resistivity of copper cold-worked at 293°K and annealed at 373°K before irradiation.

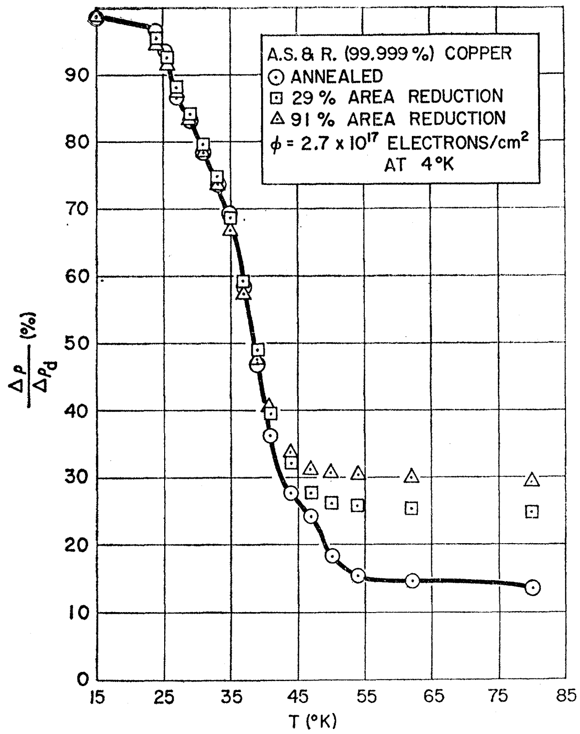

FIG. 4. Isochronal recovery of resistivity of cold-worked and annealed copper following 1-Mev electron irradiation below 10°K. The solid line follows the points for the annealed specimen.

a corresponding curve for a fully annealed specimen hereafter referred to as *A*-1. The latter curve is from previous work.[2] Isochronal recovery data, obtained following irradiation for specimens *CW*-3*a* and *A*-1, are shown in Fig. 2. The pulse time at each annealing temperature was five minutes. Isothermal recovery data for *CW*-2, *CW*-4, and *CW*-6 are plotted in Fig. 3(a) and those for *CW*-1, *CW*-3 and *CW*-5 in Fig. 3(b). In obtaining all of these data, petroleum ether was used as the annealing bath. Finally, Fig. 4 shows the isochronal recovery in Stage I for cold-worked and annealed specimens following simultaneous irradiation below 10°K with 1.0-Mev electrons; the pulse times were again five minutes. A more complete description of these latter experiments will be published later.

IV. DISCUSSION OF RESULTS

Exposure and Isochronal Recovery Curves

We shall first discuss three features of the data shown in Figs. 1 and 4. These features are the following:

(1) The resistivity increase for a given exposure to 1.25-Mev electrons at 90°K increases with the amount of cold work. The detailed shapes of the exposure curves are shown in Fig. 1.

(2) The total recovery in Stages I_D and I_E is reduced substantially by previous cold work. The magnitude of this reduction appears to increase rapidly with small amounts of cold work, then saturates with heavy cold work.

(3) The reduction in recovery in the cold-worked samples is confined almost exclusively (within 2%) to Stages I_D and I_E. Features (2) and (3) are in general agreement with the findings of Walker and Corbett.[36]

These features can be explained by the postulate that the defects responsible for Stage (I_D+I_E) recovery are retained in some manner by dislocations. More specifically, dislocations may convert the Stage (I_D+I_E) defect (i.e., the crowdion) which is mobile at temperatures below 90°K to the Stage III defect (the normal interstitial). This conversion may occur either in a dynamic manner before the crowdion has lost its kinetic energy or as a result of a chance encounter with a dislocation while the crowdion is thermally migrating through the lattice.

It should be noted that although this conversion mechanism is somewhat similar in concept to that suggested by Leibfried[37] for the displacement of atoms by the interaction of focusons with dislocation stacking faults, it differs in two important aspects. First, the total number of defects produced is enhanced in cold-worked material with Leibfried's mechanism but not with ours. Second, in our case the interstitial and vacancy are generally widely separated in the lattice, while in Leibfried's mechanism, *both* defects are produced in close proximity to the dislocation. The wide separation of the interstitial and vacancy in our case results from the transport of mass along the path of the moving crowdion, whereas in Leibfried's case, only an energy transport occurs between the site of the primary collision and the dislocation.

It might be suggested that the increased damage rate in the cold-worked specimens irradiated at 90°K is the sole result of an increased *production* rate of defects due to the enhanced dislocation concentration either by the operation of Leibfried's mechanism or as a result of a lowering of the displacement energy necessary to dislodge an atom from its lattice site in the vicinity of the dislocation core. Such an enhancement would also be observed in the 10°K damage rate, and no suppression of Stages I_D and I_E would be predicted. Our measurements have not been conclusive enough to evaluate quantitatively the influence of cold-work on the damage rate below 10°K. Walker and Corbett[36] have recently reported that the effect of cold work on the 20°K damage rate is small, which would indicate that these mechanisms play a minor role. Experiments are now in progress which should further clarify this point. In any event, these mechanisms certainly do not explain the suppression of Stages I_D and I_E by cold work as does the conversion mechanism described above.

At higher integrated flux values, the 90°K damage curves for the cold-worked samples deviate appreciably

[36] R. M. Walker and J. W. Corbett, Bull. Am. Phys. Soc. 5, 25 (1960).
[37] G. Leibfried, J. Appl. Phys. 31, 117 (1960).

from their initial linear behavior in all cases except the 92% area reduction specimens. The initial slope seems to approach a limiting value given by the slope of the 92% area reduction specimens. The integrated flux value at which the curves deviate appreciably from a linear behavior increases with increasing amount of cold work. In all probability, curves for the 92% area reduction specimens will also show a curvature at higher values of integrated flux. There is also an indication that the curvature will not continue indefinitely. It is seen in Fig. 1 that the exposure curve slope for any of the cold-worked specimens never becomes less than that characterizing the final portion of the exposure curve for A-1.

The qualitative features of the effect of cold work on the shape of the exposure curves at 90°K can be summarized as follows:

(1) All exposure curves at high integrated flux approach a slope approximately equal to that of A-1 (4.3×10^{-28} ohm-cm per e/cm^2) for 1.25-Mev electron irradiation at 90°K. (This feature is somewhat speculative since the total amount of irradiation was insufficient to precisely define the final slope.)

(2) Cold work prior to irradiation at 90°K increases the slope of the early part of the exposure curve. A limiting initial slope of about 13.3×10^{-28} ohm centimeter per e/cm^2 for 1.25-Mev electron irradiation is approached with increasing amounts of cold work.

(3) The region of integrated flux over which the transition from the initial slope to the final slope of the exposure curve occurs is shifted to higher integrated flux values with increasing amounts of cold work.

These features can be explained as follows. The *final* limiting slope at high flux values results from the direct production of immobile normal interstitials by those primary collisions in which the knock-on atom is driven in such a direction that it is not focussed into a close-packed row of atoms and therefore does not become a crowdion. The vacancy concentration in the lattice, when this slope is reached, has increased to the point where vacancies are completely dominant over dislocations as crowdion sinks and all crowdions which are produced, therefore, are annihilated at the irradiation temperature of 90°K. The limiting value of the *initial* slope corresponds to the reverse situation, in which all crowdions are being converted to normal interstitials because the dislocations dominate as sinks prior to the enhancement of the vacancy concentration by prolonged irradiation. The ratio of these two slopes therefore can be interpreted as a measure of the fraction of the displaced atoms which are produced directly as normal interstitials by 1.25-Mev electron irradiation at 90°K. This interpretation implicitly assumes that (a) the resistivity of a normal interstitial is independent of whether or not it was produced directly or by crowdion conversion, and (b) that any contribution from Leibfried's mechanism is reasonably small. In the transition region from the initial to the final slope, the shape of the exposure curve is dependent on the relative magnitudes of the capture cross sections for crowdions by vacancies and dislocations. The complex geometry of dislocations, as well as the unknown relative concentrations and spatial distribution of dislocations and vacancies, make a detailed understanding of the complete exposure curves impossible at present.

It should be noted at this point that the above explanation for the shapes of the 90°K exposure curves does not satisfactorily explain the 80°K exposure data obtained by Corbett and Walker. The final slope of their 80°K exposure curve in annealed copper is at least a factor of two and one half less than the corresponding present value. Furthermore, the shape of their exposure curve is apparently quadratic rather than linear; however, their exposure was terminated at an integrated flux value at which the linear portion of our exposure curve had just begun. The incident electron energy is somewhat different for their experiments and the present ones (1.4 Mev and 1.25 Mev, respectively), and more important, the impurity concentration in their specimens was lower than in ours ($\rho_0=1.5\times10^{-9}$ ohm-cm and 3.4×10^{-9} ohm-cm, respectively). These differences are undoubtedly important and the need for further work is indicated. The model presented by Corbett, Smith, and Walker predicts that the slope of the 80°K exposure curve will continue to decrease at higher integrated flux values whereas our model predicts a constant final slope.

The isochronal recovery data obtained following both the 10°K and 90°K irradiations are consistent with the explanation given above for the effects of cold work on the exposure curves. All of the additional resistivity change produced in the cold-worked specimens at 90°K recovers in Stage III as shown in Fig. 2; this is also the case for cold-worked specimens irradiated below 10°K but is not shown in Fig. 4. The conversion of crowdions to normal interstitials enhances the number of the latter produced in cold-worked specimens irradiated at 90°K. Therefore, the enhancement of Stage III recovery, which we ascribed to the migration and annihilation of normal interstitials, is predicted by our model. Furthermore, it is apparent that if Stage III is enhanced by such a mechanism, it must occur at the expense of Stage (I_D+I_E). The observed reduction in the magnitude of Stage (I_D+I_E) in cold-worked specimens, relative to the annealed specimen, is therefore regarded as direct experimental evidence favoring the present interpretation.

Figure 2 also shows that Stage III, as measured by the isochronal method, is shifted downward in temperature for the cold-worked specimens relative to A-1. Previously[2], an expression was derived which predicts the magnitude of the temperature shift ΔT_c of the central temperature T_c for a recovery process obeying a second-order chemical rate equation. This derivation is based on the assumption that the temperature shift results solely from the differences in the initial concentration of the defects responsible for the recovery stage and differences in the average heating rate. Use of the bimolecular rate equation cannot be justified for the cold-worked specimens for reasons described below. However, if such a calculation is made, one estimates the shift to be about 80% as large as is observed. Therefore, the fact that a shift is observed should not be construed as evidence that the additional Stage III damage in the cold-worked specimens results from a different type of defect.

Kinetics of Stage III Recovery

As discussed in a previous paper,[2] the isochronal and isothermal recovery data can be combined to determine the activation energy, E, of the recovery process. From the isothermal recovery curve, values of τ_i, annealing time, are obtained which correspond to each measured resistivity value on the isothermal curve. Values of $\Delta\tau_i$ for successive measurements, along with the appropriate temperature, T_i, are then determined. The activation energy is obtained from the slope of the curve obtained by plotting $\ln\Delta\tau_i$ vs T_i^{-1}. The value of E derived in this manner must be treated with caution since, if a chemical rate equation of constant order is not obeyed, then this method of analysis demands identical treatments for isochronal and isothermal specimens. Nevertheless, a value of $E=0.67$ ev was obtained for CW-3 and CW-3a using this method; this energy appears to characterize uniquely the recovery over a 40°K temperature range in Stage III. No unique activation energy was found for CW-5 and CW-5a. For comparison, 0.60 ev is the activation energy previously determined for A-1. We are inclined to believe that the 0.07 ev difference in the activation energy for Stage III in CW-3 and CW-3a from A-1 is due to an actual shift in the energy brought about by cold work and not simply experimental error. It is believed that this shift is an indication that the unique recovery stage is becoming more complex through interaction of the migrating interstitials with the various defects produced by the cold work. This contention seems justified to some extent by the fact that specimens CW-5 and CW-5a, which received heavier amounts of cold work, do not exhibit a unique activation energy over any appreciable temperature range in Stage III.

Previously[2] it was shown that the recovery kinetics of Stage III for A-1 could be accurately described by

$$d\rho/dt=-C(T)\rho^{\gamma}, \qquad (1)$$

with $\gamma=2.0$. In the present work, it was found that the Stage III recovery kinetics for all of the cold-worked specimens could not be described by Eq. (1) with $\gamma=2$. If such an analysis is made of the data, "best values" of γ are obtained which lie in the range 1.4 to 1.9 for the amounts of cold work used, the lower values corresponding to the greater amounts of cold work. Presumably, lattice defects produced by the cold work are responsible for this change in kinetics. The direction in which the apparent value of γ is shifted suggests that the concentration of sinks for the migrating interstitials exceeds the interstitial concentration in the cold-worked specimens.

According to our model, cold work produces lattice vacancies which are immobile in Stage III as well as the temperature at which the cold work was performed. Therefore, the data were analyzed using the following rate equation for the time rate of change of defect concentration:

$$dn_I/dt=-C'n_In_V=-C'n_I(n_I+n_0), \qquad (2)$$

where the subscripts I and V refer to interstitials and vacancies, and n_0 represents the excess vacancy concentration which was introduced by the cold work. Here it is assumed that interstitials annihilate only at vacancies. Integration of Eq. (2) gives

$$Bt=\ln[(n_I+n_0)/n_I]. \qquad (3)$$

Assuming that the measured resistivity changes are proportional to changes in the defect concentration, we may write

$$Bt=\ln[(\rho+\rho_0)/\rho]. \qquad (4)$$

The isothermal recovery data for the various cold-worked specimens were plotted in the form $\ln[(\rho+\rho_0)/\rho]$ vs t and ρ_0 was adjusted so that such a plot resulted in a straight line. In each case, values of ρ_0 above and below that value which yielded a straight line were used to show that the curvature actually progressed from a negative value through zero, corresponding to the selected value of ρ_0, to a positive value. If this behavior could not be satisfied, the analysis was assumed to fail for that particular specimen. Taking the constant relating n_0 and ρ_0 to be 1.5 micro-ohm-cm per atom percent vacancies, it was found that $n_0=5\times10^{-6}$ for CW-3 and $n_0=1.5\times10^{-6}$ for CW-1. These values of n_0 represent the excess vacancy concentration (produced by the cold work) which remains after a 30-minute anneal at 373°K. (The failure of this analysis for all other specimens will be discussed later.) Therefore, we conclude that Eq. (2) accurately accounts for the isothermal recovery data and yields very reasonable values for n_0, the residual vacancy concentration. We feel this kinetic behavior is new and convincing evidence that vacancy migration must be ascribed to Stage IV and that Stage III must result from the migration of an interstitial-type defect.

Undershoot Phenomenon

The specimens which were cold-worked and annealed at 293°K before irradiation (CW-2, 4, 6) exhibited a surprising recovery phenomenon after long time annealing at 273°K following irradiation. Under these conditions, the absolute resistivity of the cold-worked specimens was actually less than the pre-irradiation value. Figure 3(a) shows that the magnitude of this undershoot increases with increasing amounts of cold work. If the cold-worked specimens were annealed for 30 minutes at 373°K before irradiation, no appreciable undershoot occurred [Fig. 3(b)].

A separate experiment was conducted to show that the occurrence of this phenomenon is a direct consequence of encounters of migrating radiation-induced defects with certain residual defects produced by the cold work. A copper wire was reduced in area by 32% at 293°K, then isothermally annealed at 273°K for five hours, and its recovery rate compared with *CW*-4. The rate of recovery for this specimen was at least 30 times slower than that observed for *CW*-4 at the same residual resistivity value. (Further, it should be noted that this phenomenon is not to be associated with dislocation climb induced by point defect migration since this latter effect has been shown[17] to be negligibly small below about 373°K.)

The undershoot phenomenon can be qualitatively explained as follows. Seeger[27] has pointed out that various kinds of multiple vacancies, e.g., tri-vacancies, quadri-vacancies, etc., should be produced by plastic flow in metals. Let us postulate the existence of a complex vacancy of multiplicity m which is essentially immobile at 293°K and becomes quite mobile or dissociates near 373°K. (This latter feature is needed to account for the lack of undershoot in *CW*-1, *CW*-3, and *CW*-5.) When a migrating interstitial encounters such a defect, the interstitial will be annihilated and the remaining complex vacancy or vacancies will have a total multiplicity of $(m-1)$. If any of these remaining products have appreciable mobility at 273°K, they can then migrate and annihilate at sinks other than interstitials. Such a process will result in a residual resistivity recovery of greater magnitude than that corresponding to the annihilation of a Frenkel pair, assuming that the resistivity of any vacancy complex exceeds that of a single vacancy. Regardless of the specific identification of the vacancy complex, we feel that the explanation of this undershoot phenomenon requires the migration of an interstitial-type defect in Stage III.

The most obvious choice for the original complex is a tri-vacancy. When a migrating interstitial combines with this defect, the product is a highly mobile divacancy which can escape from the lattice. Our present knowledge of the mobility or dissociation temperature of tri-vacancies is inadequate to warrant the conclusion that the tri-vacancy plays the dominant role in the undershoot phenomenon but it seems to be a reasonable choice.

Since the magnitude of the undershoot increases with increasing cold work, we conclude that the number of interstitials captured by vacancy complexes relative to the number captured by singles increases with increasing cold work. Furthermore, if the vacancy complexes are present in any appreciable concentration, the Stage III recovery kinetics appear to be extremely complex. This is apparently the primary reason that Eq. (2) does not satisfactorily fit the isothermal recovery data for specimens *CW*-2, 4, 6, since it is assumed in Eq. (2) that interstitials are captured solely by single vacancies. The unsatisfactory fit for specimen *CW*-5 is most probably a result of the fact that the dislocation density in this heavily cold-worked specimen is sufficiently high so that the dislocations seriously compete with vacancies as primary sinks for the migrating interstitials.

V. CONCLUSIONS

The specific modifications and expansions of our earlier point defect recovery model for copper are summarized below.

(1) Two kinds of interstitial configurations, the crowdion and the normal interstitial, may be produced in copper by electron irradiation.

(2) Crowdions migrate in Stage $(\mathrm{I}_D+\mathrm{I}_E)$; normal interstitials migrate in Stage III.

(3) Crowdions can be converted to normal interstitials in the vicinity of dislocations.

(4) A vacancy complex, possibly a tri-vacancy, is relatively stable at 293°K and migrates or dissociates near 373°K.

VI. ACKNOWLEDGMENT

We are grateful for the assistance of H. H. Neely in performing the experimental work.