Point Defect Studies in Gold by Electron Irradiation at Low Temperatures. II. Resistivity Recovery Spectrum from 15 to 240°K†

WALTER BAUER AND A. SOSIN
Atomics International, Division of North American Aviation, Inc., Canoga Park, California
(Received 27 April 1964)

We have studied the resistivity recovery of 99.999% pure gold after 2-MeV electron irradiation near 13°K. Combining our observations on the defect-concentration dependence of the recovery with some simple calculations and other relevant experimental results, we have reached the following conclusions. In the temperature range from 15 to 50°K, the recovery consists of a spectrum of processes characterized by first-order kinetics, and therefore no random vacancy-interstitial recombination with a measurable resistivity decrease takes place. In the temperature range from 50 to 240°K, the recovery is almost continuous; long-range migration of defects is not likely. We attribute most of the resistivity recovery of gold between 15 and 240°K after electron irradiation to the nonrandom recombination of Frenkel pairs.

I. INTRODUCTION

IN an earlier paper[1] (to be referred to as I) on point defect studies in gold, we presented experimental data related to the cross section for displacement of atoms by electrons, and to the minimum energy required to displace atoms—the threshold displacement energy T_d. We concluded on the basis of these and related data, and on the basis of some simple calculations, that for electron energies less than 2 MeV (maximum energy transferred to a gold atom, $T_m<66$ eV), the production of direct displacements is primarily confined to the ⟨100⟩ direction in gold, whereas in copper, for the equivalent energy range (less than 1 MeV), displacements occur in both the ⟨100⟩ and ⟨110⟩ directions.

If different interstitial configurations are produced by displacements in the ⟨100⟩ and ⟨110⟩ directions, one would expect the recovery of electrical resistivity during post-irradiation annealing to be different in gold and copper. This assumes that the activation energies of migration of the same defects in gold and copper are comparable. We have studied the recovery in gold in some detail and present our results here. The recovery in the temperature range from 15 to 240°K is discussed in this paper, and the recovery in the temperature range from 240 to 340°K will be discussed in a subsequent paper. The recovery of damage in gold from 15 to 240°K has been studied previously after electron[2,3] and deuteron[4,5] irradiations of pure gold. The major observations of these investigations are:

1. The resistivity recovery from 8 to 220°K in gold is appreciably less than in copper and silver. In annealed copper, for example, in stage I ($T<60$°K) 85 to 90% of the electrical resistivity increase due to irradiation is recovered, whereas in gold, only 20% is recovered. The recovery in stage II (60°K$<T<240$°K) in pure copper is less than 5%, whereas in gold, 30% of the resistivity recovers.

2. No well-defined recovery peaks with recovery larger than 10% are present in gold from 15 to 240°K. In contrast, the stage I recovery in copper consists of of a series of reasonably well-defined peaks with substantial recovery.

The experiments described in this paper were performed to identify the resistivity recovery processes after electron irradiation. The use of electrons with energies of 2 MeV in our experiments is dictated by the fact that the damage produced is particularly simple. The damage consists almost entirely of vacancy-interstitial pairs, of varying separation, with very few multiple displacements, and no thermal or displacement spikes. Thus, the interpretation of the results is not complicated by the creation of any sizeable concentration of divacancies or higher order vacancy clusters or di-interstitials during the irradiation. Similarly, effects due to spikes, created in heavy particle irradiation, are absent.

The experimental methods are described in part II. In part III we discuss the characteristics of the recovery spectrum. Part IV deals with the experimental results and discussion of the recovery from 15 to 50°K. Part V deals with the experimental results and discussion of the recovery from 50 to 240°K.

II. EXPERIMENTAL METHODS

The procedures for specimen preparation and for irradiation near 13°K have been described in detail in I. The residual resistivities of the various specimens are listed in Table I. In order to anneal simultaneously two specimens with different amounts of damage following irradiation, one specimen was completely shielded from the electron beam during part of the irradiation. This was accomplished by inserting a $\frac{1}{8}$-in.-thick copper plate in front of one specimen. One end of the plate was soldered to an iron rod which allowed the plate to be moved magnetically, using a relay coil. The plate was free to slide on an inclined bracket so that the plate slid down the incline, under the action of gravity, when

* This work was supported by the U. S. Atomic Energy Commission.
[1] W. Bauer and A. Sosin, Phys. Rev. (to be published).
[2] J. B. Ward and J. W. Kauffman, Phys. Rev. 123, 90 (1961).
[3] W. Bauer, J. W. DeFord, J. S. Koehler, and J. W. Kauffman, Phys. Rev. 128, 1497 (1962).
[4] H. G. Cooper, J. S. Koehler, and J. W. Marx, Phys. Rev. 97, 599 (1955).
[5] K. Herschbach, Phys. Rev. 130, 554 (1963).

TABLE I. Experimental results.

Run	Remarks	Specimen	Residual resistivity ($\times 10^{-9}$ ohm-cm)	Damage ($\times 10^{-9}$ ohm-cm)	Range of recovery studied
I	0.002-in.-diam wire	1	4.15	1.56	15–45°K
		2	4.09	7.29	
II	Same specimens as run I (increase in ρ_0 due to slight cold work)	1	4.71	0.352	15–220°K
		2	4.68	2.65	
III	0.00025-in.-thick foil	1	5.33	2.22	15–330°K
		2	5.38	0.645	
IV	Same specimens as run III	1	5.12	1.85	15–240°K
		2	5.65	1.50	
V	0.002-in.-diam wire $\Delta\rho_{\text{quench}}=2.8\times10^{-9}$ ohm-cm	1	3.65	4.61	15–240°K
		2	3.06	5.69	

the magnet was turned off, thereby shielding one specimen. No resistivity increase was observed in the shielded specimen during the irradiation.

In-place quenching of one of the specimens before irradiation was accomplished as follows. The cryostat was filled with nitrogen gas near room temperature and the specimen was heated to approximately 680°C by passing an electrical current through it. Then the current was shut off, the nitrogen gas pumped out, and liquid nitrogen admitted into the lower reservoir. This type of quench is rather slow in comparison with standard quenching techniques. Thus, a considerable concentration of divacancies and larger vacancy complexes may have been formed during the quench. This, however, does not influence the main conclusions drawn from the experiment.

III. CHARACTERISTICS OF RECOVERY SPECTRUM

It is assumed that the value of a macroscopic quantity such as resistivity depends directly on the concentration of defects present in the lattice. As the temperature of the specimen is raised, a resistivity decrease is generally observed. Our analysis of recovery data will be based on the kinetic equation

$$dn/dt=-KnP\exp(-E/kT), \tag{1}$$

where n is the concentration of defects which are annihilated or trapped in a process characterized by an activation energy E. The function P is the concentration of sinks for annihilation or of traps. The other quantities are the annealing temperature T, Boltzman's constant k, and a vibrational frequency constant K.

TABLE II. Calculated temperature shifts.

Run	Temperature shift $30<T<40$ $E\approx0.1$ eV	Temperature shift $150<T<180$ $E\approx0.4$ eV
I	1.6°K	9°K
II	1.9°K	11.8°K
III	1.3°K	7.3°K
V	1.3°K[a]	5.1°K[a]

[a] These values are lower limits since n_0 was chosen to be 0.5 of the original concentration of interstitials for $E\approx0.1$ eV and 0.7 of the original concentration of interstitials for $E\approx0.4$ eV.

The activation energy for migration of interstitials to vacancies is effectively lowered when the elastic interaction energy, which exists between two centers of dilatation, is attractive. (An additional factor involving the orientation should be included and may modify this simple argument.) The value of the interaction energy depends inversely on the third power of their separation[6] so that the closest Frenkel pairs are expected to recover at the lowest temperatures in a correlated manner and first-order kinetics apply (i.e., P is a constant near unity). For processes involving random interstitial-vacancy recombination at higher temperatures, $P=n_v$, the vacancy concentration. (In this discussion we assume that the interstitial is the migrating entity.) Since electron irradiation results in the creation of an equal number of interstitials and vacancies, $n=n_v$. For our experiments we can rewrite Eq. (1) as

$$dn/dt=-Kn^{\gamma}\exp(-E/kT), \tag{2}$$

where γ is unity for close pair or correlated recovery and $\gamma=2$ for random vacancy-interstitial recombination.

If an excess concentration of vacancies v_0 exists during the random vacancy-interstitial recombination process (due to pre-irradiation quenching, for example), the appropriate kinetic equation is

$$dn/dt=-K(n^2+nv_0)\exp(-E/kT). \tag{3}$$

Recent modulus measurements (made during the progress of our experiments) on irradiated gold performed in this laboratory[7] indicate that no long-range migration of interstitials to dislocations occurs below 180°K, further indicating that any interstitial migration in gold below 200°K is restricted to annihilation of interstitials at vacancies or trapping of interstitials by impurities. Although a substantial interaction may exist between impurities and interstitials,[8] in the pure samples used in the present experiments, we would expect

[6] J. D. Eshelby, Acta Met. 3, 487 (1955).
[7] D. W. Keefer and A. Sosin, Bull. Am. Phys. Soc. 9, 282 (1964).
[8] A. Sosin and H. H. Neely, Phys. Rev. 127, 1465 (1962).

TABLE III. Experimental results on copper.[a]

Damage (ohm-cm) at 20°K	Approximate temperature of I_E peak	Shift of I_E peak temperature with respect to low-damage case	Calculated temperature shift. See Appendix. (°K)	Fractional recovery at 48°K	Damage (ohm-cm) at 80°K	Fractional recovery of $\Delta\rho = 2.73\times10^{-10}$ ohm-cm resistivity introduced at 20°K as measured after 2 h at 52.7°K.
3×10^{-10}	51°K	0	0	75%	0	86%
1.8×10^{-9}	49°K	2°K	3.2°	81%	0.35×10^{-10}	88%
5.5×10^{-9}	47°K	4°K	5°	85%	1.35×10^{-10}	94%

[a] See Ref. 9.

only a small fraction of the interstitials to become trapped. Thus, we expect direct vacancy-interstitial annihilation to dominate the recovery process. The experiments described here confirm this interpretation of the recovery processes.

A simple approach toward identifying recovery processes fundamentally more complicated than close pair recombination (i.e., to locate a process involving random vacancy-interstitial recombination) is to examine the recovery spectrum for evidence of a shift in the temperature of an "annealing peak" with defect concentration. It is shown in the Appendix that the temperature T_c of a recovery peak, as measured in an isochronal annealing treatment, and associated with close pair recombination ($\gamma=1$), is independent of the concentration of defects. (T_c is precisely defined in the Appendix.)

The temperature of the recovery peak associated with random vacancy-interstitial recombination ($\gamma=2$) depends on the concentration of defects. An expression for the expected temperature shift for the two types of experiments described here is developed in the Appendix. In the first type of experiment, differing concentrations of damage were introduced into two closely identical specimens. In the second type of experiment, an excess concentration of vacancies was introduced into one of the specimens prior to the irradiation; then an approximately equal concentrations of defects were introduced in both specimens by irradiation. Numerical values of the temperature shifts predicted for a recovery peak associated with random vacancy-interstitial recombination for the two types of experiments are listed in Table II.

To demonstrate the reliability of these calculated temperature shifts, we made similar calculations for the case of copper and compared them with the experimental results of Corbett *et al.*[9] on copper. They used two methods to achieve differing concentrations of vacancies. In the first method, they irradiated their samples to differing amounts of integrated flux near 20°K and studied the subsequent recovery. The second method consisted of irradiations at 80°K prior to the 20°K irradiation. This results in an excess concentration of vacancies because interstitials mobile below 80°K are annihilated during the irradiation. Their experimental results and the expected temperature shift as calculated from the equations of the Appendix are summarized in Table III. These experimental results in copper are in marked contrast to the present data in gold, since, as pointed out in the next section, no temperature shifts have been observed in gold from 15 to 50°K.

[9] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. 114, 1460 (1959).

IV. RECOVERY FROM 15 TO 50°K

A total of five irradiations near 13°K were carried out. The various resistivities and temperature ranges of recovery are summarized in Table I. In each irradiation, two specimens were irradiated simultaneously. Different defect concentrations were produced in the two specimens irradiated (and annealed) simultaneously, as described in part II of this paper. This method eliminated artificial differences in recovery between the specimens due to temperature or time variations and, therefore, comparison between the different specimens in each run are more meaningful than between specimens of different runs. In runs I, II, and III (Figs. 1, 2, and 6), a different amount of damage was introduced by the shutter method. In run V (Fig. 3), one of the specimens was prequenched, as described in part II. In run IV (Fig. 5), approximately equal amounts of damage were introduced to investigate differences in recovery due to intrinsic differences in the specimens. In these experiments the fractional recovery was measured after 10-min pulses at successively higher temperatures.

The recovery measurements from 15 to 50°K of runs I, II, and V are shown in Figs. 1, 2, and 3. The slope of the fractional recovery of run I, together with the experimental results of Ward and Kauffman,[2] is shown in Fig. 4. Although they used 2.5-MeV electrons, the average energy of the electrons was only 2.2 MeV since they used 0.008-in.-diam gold wires. The most important results to be observed are:

1. The maximum difference in recovery between pairs of specimens is a few percent. This difference is larger than the experimental error, which is of the order of a few tenths of a percent. We attribute this mainly to intrinsic differences in the samples (see Fig. 5). For example, different crystallographic orientations in the individual grains of the polycrystalline specimens,

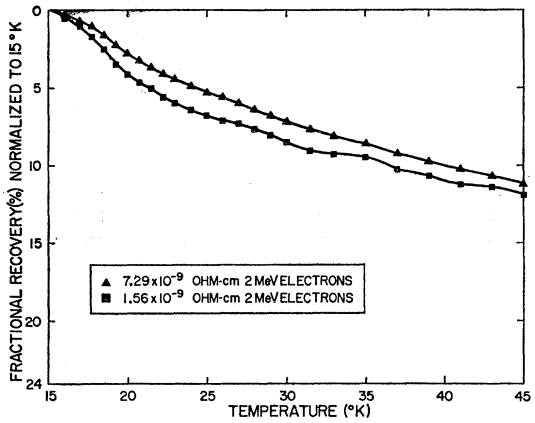

FIG. 1. The resistivity recovery as a function of annealing temperature in run I of a pair of specimens irradiated to differing integrated electron fluxes (the irradiation damage is indicated in box). The specimens were annealed simultaneously for 10 min at each temperature.

coupled with a strong dependence of the displacement process upon crystallographic orientation, could result in different populations of various Frenkel pair configurations. Thus, one cannot attach any significance to the small differences in the recovery pattern between 15 and 30°K of run II.

2. There is no significant increase in recovery with more damage in runs I and II; indeed, the more heavily damaged specimens recovered slightly less. This suppression of close pair recovery with a larger concentration of defects could be due to long-range interaction between interstitials tending to decrease the effects to vacancies.

3. There is no meaningful shift in the temperature of any recovery stage as a function of defect concentration, as can be seen in Fig. 4.

4. The excess concentration of vacancies produced by the prequenching of one of the specimens seems to have no effect on the recovery, as can be seen in Fig. 3, although the temperature shift expected in run V is 1.3°K (Table II). The amount of recovery associated with random interstitial-vacancy annihilation should depend strongly on the concentration of vacancies. This is especially the case if there is interstitial clustering or some trapping of interstitials by impurities. We note that in copper (see Table III) an excess concentration of

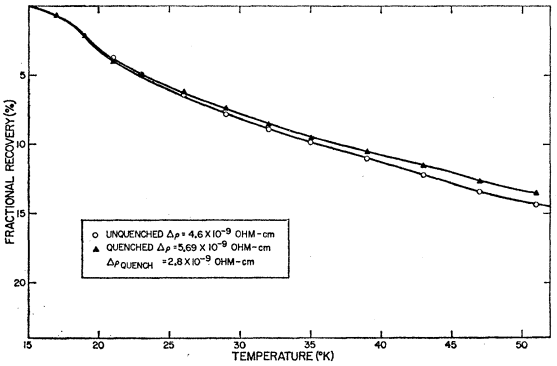

FIG. 3. The resistivity recovery as a function of annealing temperature in run V of a pair of specimens irradiated to approximately the same integrated electron fluxes. One of the specimens was quenched prior to the irradiation. The irradiation damage and quenched-in resistivity is indicated in box. The specimens were annealed simultaneously for 10 min at each temperature.

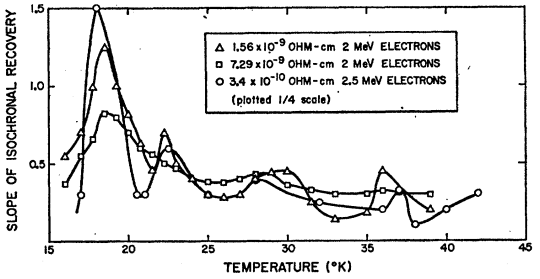

FIG. 4. The slope of the resistivity recovery as a function of annealing temperature. The data points of run I in which the specimens were annealed simultaneously are indicated as triangles and squares. The experimental results of Ward and Kauffman plotted to $\frac{1}{4}$ scale are shown as circles. The irradiation damage of the specimens is indicated in the box.

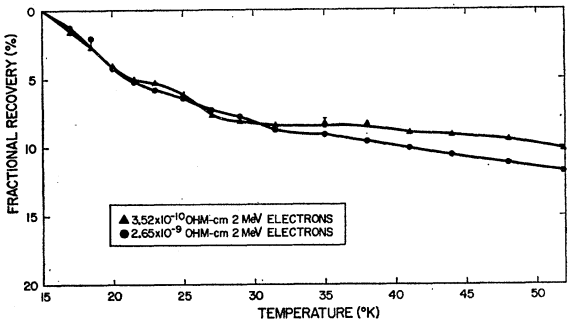

FIG. 2. The resistivity recovery as a function of annealing temperature in run II of a pair of specimens irradiated to differing integrated electron fluxes (the irradiation damage is indicated in box). The specimens were annealed simultaneously for 10 min at each temperature.

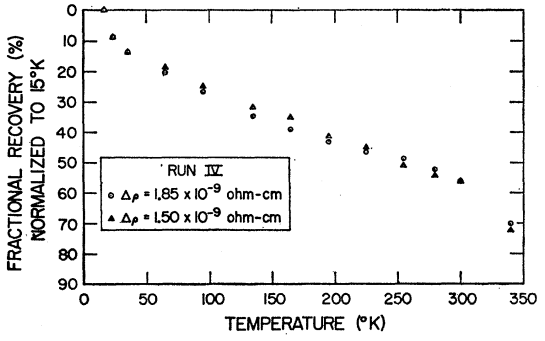

FIG. 5. The resistivity recovery as a function of annealing temperature in run IV of a pair of specimens, irradiated to approximately the same integrated electron fluxes (the irradiation damage is indicated in box). The specimens were annealed simultaneously for 10 min at each temperature.

vacancies comparable to the radiation-induced amount resulted in an enhancement of the recovery by 8%.

In summary, no meaningful temperature shift or change in fractional amount of recovery can be associated with any recovery peak for differing concentrations of damage in gold. Similarly, an excess concentration of vacancies has no effect on the amount of recovery. These results are in marked contrast with the corresponding results in copper. Thus, we conclude that it is very unlikely that a defect configuration exhibiting recovery kinetics characterized by an order of reaction greater than one and producing a measurable resistivity contribution annihilates in the temperature range 15 to 50°K.

V. RECOVERY FROM 50 TO 240°K

The recovery studies in this temperature range were conducted in the same manner and with the same objective as those described in the last section. In presenting the results in a separate section, we do not want to imply that there is basically a different mechanism responsible for the recovery than there is below 50°K. Indeed, we propose that the recovery of gold from 50 to 240°K is due to the same basic mechanism as the recovery below 50°K. The division into these temperature regions is retained to conform to the stage I and II divisions generally observed in other metals (e.g., copper).

The results of the recovery studies are shown in Figs. 5–8. The slopes of the fractional recovery curves (in arbitrary units) as a function of temperature are shown in Fig. 9. One can make several observations from the experimental results:

1. In Fig. 5, the recovery, after irradiation to almost equal damage in both specimens is shown. The differences in the recovery of the two specimens are considerably larger from 70 to 240°K than below 70°K.

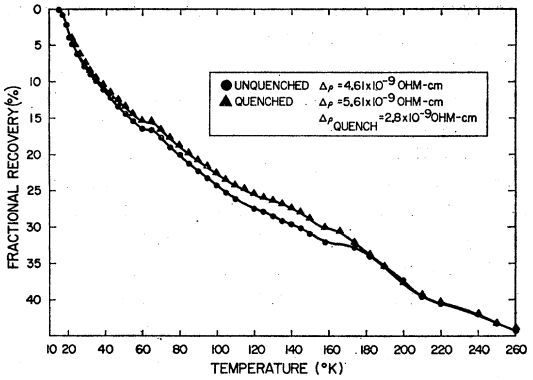

FIG. 8. The resistivity recovery as a function of annealing temperature in run V of a pair of specimens irradiated to approximately the same integrated electron fluxes. One of the specimens was quenched prior to the irradiation. The irradiation damage and quenched-in resistivity is indicated in box. The specimens were annealed simultaneously for 10 min at each temperature.

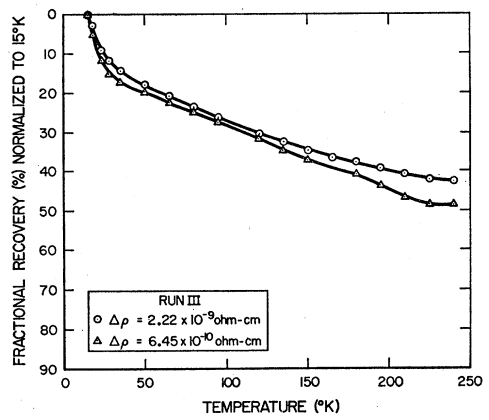

FIG. 6. The resistivity recovery as a function of annealing temperature in run III of a pair of specimens irradiated to differing integrated electron fluxes (the irradiation damage is indicated in box). The specimens were annealed simultaneously for 10 min at each temperature.

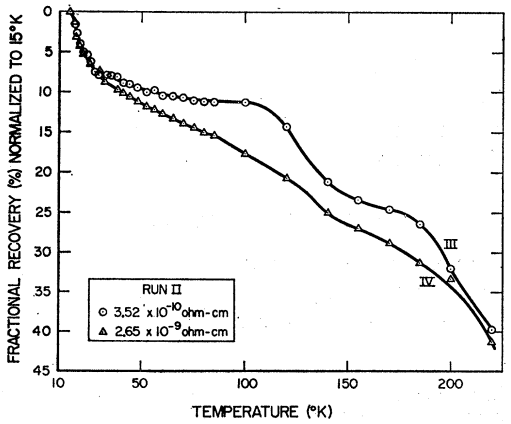

FIG. 7. The resistivity recovery as a function of annealing temperature in run II of a pair of specimens irradiated to differing integrated electron fluxes (the irradiation damage is indicated in box). The specimens were annealed simultaneously for 10 min at each temperature.

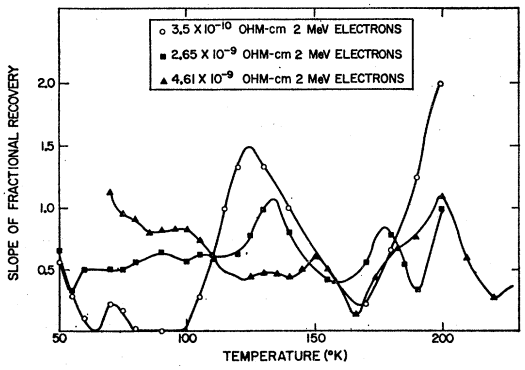

FIG. 9. The slope of the resistivity recovery as a function of annealing temperature. The data points of run II, in which the specimens were annealed simultaneously, are indicated as circles and squares. The data points of the unquenched specimen of run V are shown as triangles. The irradiation damage of the specimens is indicated in the box.

This suggests that the dependence of the recovery on intrinsic differences in the specimens (such as different orientations of the grains of the polycrystalline material) is more pronounced from 50 to 240°K than at lower temperatures. Such differences in recovery cannot be traced readily to differences in impurity content or cold work between the two specimens since the specimens were prepared from the same starting material and the annealing procedure for both was identical.

2. There is no significant dependence of the amount of recovery on the concentration of damage as can be seen in Figs. 6 and 7. Although differences in recovery between the two specimens exist in each run, the dependence of the amount of recovery on the concentration of defects is reversed in runs II and III. We can only attribute this somewhat anomalous behavior of the recovery to intrinsic differences in the two specimens.

3. The recovery after irradiation of the unquenched and prequenched specimens is shown in Fig. 8. One notes that the recovery of the prequenched specimen is not significantly enhanced; indeed, the recovery of the unquenched sample seems to be larger.

4. The slopes of the fractional recoveries observed in run II and in specimen 1 of run V are shown in Fig. 9. One notes that, while a spectrum of minor recovery peaks is evident, there are no well defined peaks which can be readily identified in the recovery of the various specimens. The recovery associated with any one annealing peak is less than 10% and the error in the magnitude of the slope is approximately 20%. Thus, although the expected temperature shift of a recovery peak associated with random migration is typically 12°K for run II (see Table II), we cannot resolve any significant shift in temperature of any one recovery peak.

In summary then, the recovery of electrical resistivity in gold proceeds in an almost continuous fashion from 50 to 240°K. One would expect that, if the free migration of the interstitial occurred in this temperature range, there would exist a recovery peak (or several, as is the case in copper near 45°K) with which a substantial fraction of the total recovery was associated. The absence of any well-defined, major recovery peaks is consistent with the free migration of an interstitial only if the interstitial is trapped by impurities or clusters rather than being annihilated, or if it has a negligible resistivity contribution and annihilates at sinks other than vacancies.

As mentioned in Sec. III, recent modulus measurements on irradiated gold performed in this laboratory[7] indicate that no long-range migration of interstitials to dislocations occurs below 180°K. Similar measurements on copper clearly indicate long-range migration.[10] The simplest interpretation of these results, previous resistivity data for copper, and the present resistivity data in gold is that no free interstitial migration occurs in electron-irradiated gold below 240°K,[11] while such migration does occur in copper. The simplest explanation consistent with the resistivity recovery data presented here is to attribute the recovery up to 240°K to the annihilation of close pairs. Since the recovery is almost continuous, this explanation requires that these (first order) annealing processes, characterized by a spectrum of different activation energies, overlap in temperature. If one assumes that the half-width δT of a first-order annealing peak is $T/10$, as is typically observed experimentally, the minimum number N of first-order annealing processes is roughly

$$N=\int_{15}^{240}\frac{dT}{T/10}=28. \tag{4}$$

It has been shown[12] that in the split interstitial recovery spectrum there may be 23 different annealing processes associated with Frenkel pair separations of less than 2.5 lattice constants. It is not obvious, *a priori*, that these 23 processes are all energetically different, and that they span a range of activation energies from 0.05 to 0.6 eV.[13] However, there is a sufficient number of possible different Frenkel pair configurations within a slightly larger sphere, of radius 15 Å say, such that although not all configurations are energetically distinct, the condition of Eq. (4) may easily be fulfilled.

The recovery spectrum of gold below 60°K after irradiation with 10-MeV deuterons[5] is similar to that after electron irradiation with the exception that a recovery peak occurs near 33°K, which is not present after electron irradiation. Clearly, enough energy is available for the production of crowdions in deuteron irradiations, but the amount of recovery associated with the 33°K peak is only a few percent. Thus, if crowdions are mobile below 60°K, they are produced only in small concentrations at high values of T_m, if at all.

In conclusion, we feel that in gold, most of the resistivity recovery below 240°K after 2-MeV electron irradiation is due to the annihilation of close Frenkel pairs, and that random interstitial-vacancy migration occurs in the temperature range 240 to 340°K (stage III). This topic will be discussed in a subsequent paper.

ACKNOWLEDGMENTS

The experimental assistance of W. Goeppinger is gratefully acknowledged. The authors wish to thank John Brinkman for many valuable suggestions.

[10] D. W. Keefer and A. Sosin, Appl. Phys. Letters 3, 185 (1963).

[11] The temperatures corresponding to pinning stages in modulus measurements may be considerably lower than the corresponding stages in resistivity recovery.

[12] J. S. Koehler and G. Leibfried, J. Phys. Soc. Japan, Suppl. III, 18, 266 (1963).

[13] The activation energies 0.05 and 0.6 eV correspond to processes annealing near 15 and 240°K, respectively.

APPENDIX

One identifies the temperature at which the rate of recovery in a particular process is a maximum as T_c. This is determined by locating the inflection point of the fractional recovery curve as a function of temperature. Using the notation of Eq. (2),

$$[d^2n(T)/dT^2]_{T=T_c}=0. \quad \text{(A1)}$$

Assuming that the temperature is varied simply with time, we take time as the independent variable.

Then,

$$[d^2n/dt^2]_{T=T_c} =[dn/dt]_{T=T_c}[(dT/dt)^{-1}]_{T=T_c}[d^2T/dt^2]_{T=T_c}. \quad \text{(A2)}$$

Combining Eqs. (2) and (A2), we have

$$-\gamma n_c^{\gamma-1}K\exp(-E/kT_c)+(E/kT_c^2)[dT/dt]_{T=T_c} =[(dT/dt)^{-1}(d^2T/dt^2)]_{T=T_c}, \quad \text{(A3)}$$

where n_c is the concentration of those defects responsible for the particular recovery stage characterized by the unique activation energy E existing after the anneal at the temperature T_c. For purposes of illustration, we assume a typical annealing schedule $T=T_0+At$. Then Eq. (A3) becomes

$$-\gamma n_c^{\gamma-1}K\exp(-E/kT_c)+(E/kT_c^2)A=0. \quad \text{(A4)}$$

As can be seen readily from Eq. (A4), the value of T_c is independent of n_c for first-order processes ($\gamma=1$).

For $\gamma>1$, the value of T_c will be some function of n_c. To simplify the comparison with experiment it is necessary to relate n_c to n_0, the initial concentration of defects of activation energy E.

We derive an expression relating n_0 to n_c for the case of free interstitial migration to vacancies in the presence of an excess concentration of vacancies v_0. We assume a constant heat-up rate $dT=Adt$. From Eq. (3), we have

$$dn/dT=-(K/A)(n^2+v_0n)\exp(-E/kT). \quad \text{(A5)}$$

Integrating Eq. (A5), and using the results of Meechan and Brinkman[14] with the approximation $E/kT_c>1$, we get

$$v_0^{-1}\ln\left[\left(\frac{n_0}{n_c}\right)\left(\frac{n_c+v_0}{n_0+v_0}\right)\right]=\frac{K}{A}\frac{kT_c^2}{E}\exp(-E/kT_c). \quad \text{(A6)}$$

In order to relate the right side of Eq. (A6) to n_c and n_0, we differentiate Eq. (A5) with respect to T and evaluate the condition at the inflection point. This results in

$$(2n_c+v_0)^{-1}=(K/A)(kT_c^2/E)\exp(-E/kT_c). \quad \text{(A7)}$$

Equating the left sides of Eqs. (A7) and (A6), we have

$$v_0^{-1}\ln\left[\left(\frac{n_0}{n_c}\right)\left(\frac{n_c+v_0}{n_0+v_0}\right)\right]=(2n_c+v_0)^{-1}. \quad \text{(A8)}$$

We now consider the two limiting cases of Eq. (A8): (a) pure second-order kinetics ($v_0\to 0$), (b) pure first-order kinetics ($v_0\gg n_c$). For condition (a), Eq. (A8) reduces to

$$\ln[1+(v_0/n_c)]-\ln[1+(v_0/n_0)]=v_0/(2n_c+v_0). \quad \text{(A9)}$$

Expanding the natural logarithms and simplifying, we have

$$n_c\simeq\tfrac{1}{2}n_0. \quad \text{(A10)}$$

For condition (b), Eq. (A8) reduces to

$$n_c=(1/2.7)n_0. \quad \text{(A11)}$$

We now develop an approximate expression relating the shift in temperature ΔT of the annealing peak associated with random interstitial-vacancy recombination for the following cases:

(a) Different initial concentrations of damage and no excess concentration of vacancies in one specimen, and (b) approximately the same initial concentration of damage, but an excess concentration of vacancies in one specimen. For case (a) we quote the results of Meechan and Brinkman,[14]

$$E/kT_c^2=2(K/A)n_c\exp(-E/kT_c). \quad \text{(A12)}$$

Combining Eq. (A12) and Eq. (A10) with differing initial concentrations of damage, n_{01} and n_{02}, we have

$$\Delta T\simeq(kT_c^2/E)\ln(n_{01}/n_{02}), \quad \text{(A13)}$$

where $\Delta T=T_{c2}-T_{c1}$ and $T_c^2\simeq T_{c1}T_{c2}$. This is the equation used to calculate the values of ΔT in Table II for runs I, II, and III, and the values of ΔT for copper in Table III. The values of ΔT for copper are in reasonably good agreement with the observed values of ΔT.

In case (b) the temperature at the inflection point of the recovery of the specimen without the excess concentration of vacancies is given by (A12):

$$(K/A)2n_{c2}=(E/kT_{c2}^2)\exp(E/kT_{c2}). \quad \text{(A14)}$$

The temperature at the inflection point of the recovery of the specimen with the excess concentration of vacancies is given by (A7):

$$(K/A)(2n_{c1}+v_0)=(E/kT_{c1}^2)\exp(E/kT_{c1}). \quad \text{(A15)}$$

The subscript 1 refers to the prequenched specimen and 2 to the unquenched one.

Dividing Eq. (A15) by Eq. (A14), and using the approximation $n_{c1}\approx n_{c2}\approx n_0/2$, which is valid for our experimental results, we have

$$\ln\left(\frac{n_0+v_0}{n_0}\right)\frac{kT_c^2}{E}\simeq\Delta T. \quad \text{(A16)}$$

Equation (A16) was used to calculate the values of ΔT for run V in Table II.

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