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Influence of Foreign Solute Atoms on Stage I Recovery in Electron-Irradiated Copper*

A. Sosin and H. H. Neely
Research Division, Atomics International Division of North American Aviation, Canoga Park, California

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Additions of 0.1 at.% Be, 0.1 at.% Ag and 0.03, 0.1, 0.3, and 1.0 at.% Au in copper are observed to suppress recovery of electrical resistivity in stage I (below 60°K) following electron irradiation. The effects of Ag and Au are essentially the same; Be is considerably more effective in suppressing stage I recovery. The effects of composition of Au is evaluated. It appears from this evaluation that close-pair recombination is accomplished with only one or two jumps, on the average, and that other recovery processes in stage I involve appreciably more jumps. The number of potential trapping sites associated with each Au atom appears to be over 30 and may approach 100.

INTRODUCTION

In a previous publication,[1] the dependence on incident electron energy of the character of resistivity recovery in pure copper in stage I (60°K) following irradiation was reported. A conclusion reached in that report was that the separation distance between the lattice site at which the original transfer of energy between the bombarding electron and a copper atom and the average position of the resulting interstitial atom is relatively large even for the case of electron-to-atom transfer energies near the minimum (threshold) energy for atomic displacement. If this conclusion is valid, and if the interaction between interstitials and foreign solute atoms is reasonably strong, dilute concentrations of solute additions should be effective in altering the recovery spectrum. Furthermore, analysis of the manner in which the spectrum is altered should yield information as to the distribution of interstitial-vacancy separations, as well as providing an insight into the nature of interstitial-solute interaction.

In order to explore these various possibilities, we have studied the recovery of resitivity in copper following irradiation at ~5°K. The variables in the experiment are type of solute addition, concentration of solute addition, and energy of incident electrons.

The earliest investigation similar in nature to ours is that of Blewitt, Coltman, Klabunde, and Noggle.[2] They neutron irradiated copper doped with 0.1 and 1.0 at. % of zinc (1.33 Å), beryllium (1.13 Å), gold (1.44 Å), silicon (1.17 Å), and nickel (1.24 Å) and studied recovery of electrical resistivity up to 250°K. (The numbers in parentheses indicate atomic radii; the atomic radius of copper is 1.28 Å). They observed the following effects, related to our results. First, nickel has little effect on the annealing spectrum; all the other dopants suppress recovery in the stage I recovery region. Since the atomic size of copper and nickel are almost equal, an important factor in the ability of a foreign solute atom to affect annealing appears to be the difference in atomic radii between it and copper, whether this difference is positive or negative.

Blewitt *et al.* also observed that, while a heavy concentration always gave more suppression, the amount of suppression, defined more formally later, is not linearly dependent on the concentration of solute addition. This observation is not particularly surprising, but the nature of the dependence is certainly important. Finally, they observed some "anomalies" in the form of resistivity increases. The Cu–1.0 at. % Si sample resistivity initially increased and proceeded to decrease only above stage I. The Cu-Be alloys showed somewhat smaller resistivity increases at about 175 to 200°K. These increases remain largely unexplained.

A related set of experiments has been conducted recently by Martin.[3] Martin's experiments were studies of electrical resistivity recovery following elec-

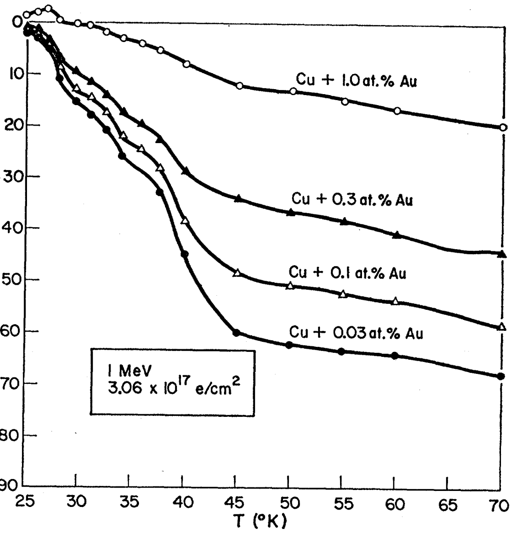

Fig. 1. Isochronal resistivity recovery spectra of gold-doped copper following irradiation at 4.2°K with electrons of 1.0 MeV incident energy as a function of gold concentration.

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[1] A. Sosin, Phys. Rev. **126**, 1698 (1962).

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

[3] D. G. Martin, Phil. Mag. **6**, 839 (1961); Atomic Energy Research Establishment Report AERE–R3843, 1961 (unpublished).

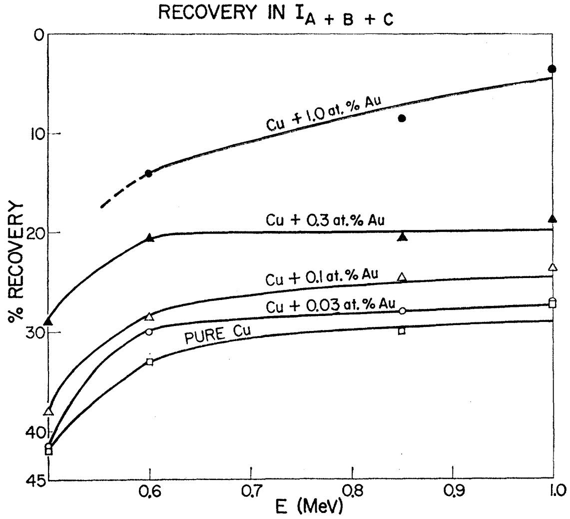

FIG. 2. Resistivity recovery in the "close pair" substages as a function of incident electron energy E for several different concentrations of gold in copper.

tron or neutron irradiation at liquid nitrogen temperature. Martin has shown that two new substages of recovery, which we shall call II_b and II_c, are introduced above liquid nitrogen temperature by additions of Ag (1.44 Å), Cd (1.52 Å), or Be. We have obtained similar results and, furthermore, have found that still a third recovery substage II_a, at about 60°K, is introduced in Cu doped with Au. (Some indication of existence of substage II_a may be observed in Fig. 1.) The detailed character of substage II_a is being investigated presently.

EXPERIMENTAL DETAIL AND RESULTS

The work reported here consists of irradiation at 4.2°K and subsequent annealing in vacuum following electron irradiation below 1.2 MeV. The techniques involved are identical with those reported elsewhere.[4] Four samples were irradiated simultaneously. Each sample was 0.0021 in. in diameter and approximately 0.5 in. long. Some additional information is given in Table I. The same samples were irradiated in sequential experiments at different electron energies. Each experiment included an annealing study, terminating at room temperature or above. Since the resistivity was always observed to return very closely to its pre-irradiation value, there would appear to be no reason to suspect that the results of a later experiment was prejudiced by an earlier experiment. Since the defect concentration injected by irradiation ($\sim 10^{-5}$) is substantially smaller than the concentrations of solute additions in any sample, no such effects should be expected.

TABLE I. Residual resistivity ρ_0 of samples used in this investigation.

Material	ρ_0 ($10^{-8}\Omega$-cm)
Cu	0.5
Cu+0.1 at. % Be	7.6
Cu+0.1 at. % Ag	3.4
Cu+0.03 at. % Au	3.4
Cu+0.1 at. % Au	6.8
Cu+0.3 at. % Au	16.7
Cu+1.0 at. % Au	56.4

Figure 1 presents the results of the study of recovery of electrical resistivity in gold-doped copper following irradiation at 1.0 MeV (incident electron energy). Several features should be noted. First, the recovery of resistivity is increasingly suppressed throughout stage I as the gold concentration is increased. Second, there appears to be a distinct recovery in the region of 65°K. In this study, datum points were taken rather far apart in this temperature region; later work shows that, indeed, another substage may be resolved. Third, the resistivity increases occur at the lowest temperatures in the 1.0 at. % alloy. Fourth, suppression is effected by the solute atoms, even in concentration of 0.1 at. %, in the close-pair annihilation region (<35°K).

A series of such experiments were conducted with these samples in which the incident electron energy was varied. The suppression of recovery persists. The experiments are summarized in Figs. 2 and 3. Data from previous experiments on pure copper are included. The abscissa in each figure is the value of incident electron energy. The average electron energy, appropriate for resistivity experiments on our wires, is about 50 keV less.

The data in Fig. 2 has been taken from the recovery curves at 35°K. This should be a reasonable indication, then, of the amount of recovery in all of the "close pair" stages, usually called substages I_a, I_b, and I_c.[5] Since the

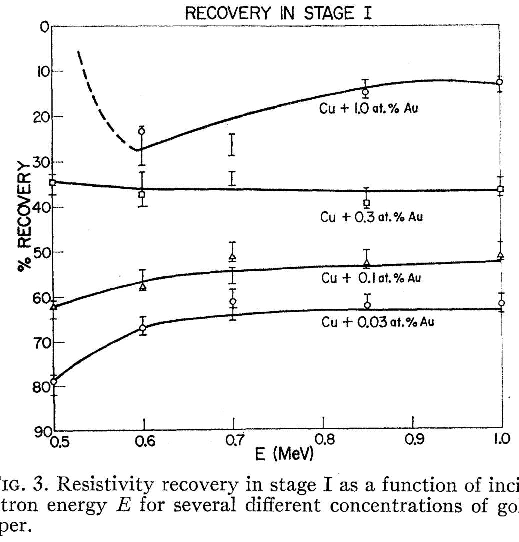

FIG. 3. Resistivity recovery in stage I as a function of incident electron energy E for several different concentrations of gold in copper.

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[4] A. Sosin and H. H. Neely, Rev. Sci. Instr. 32, 922 (1961).

[5] Substages I_a, I_b, and I_c in pure copper generally are accepted to be due to recombination of interstitials with vacancies so close that such recombination is inevitable. Substages I_d and I_e usually

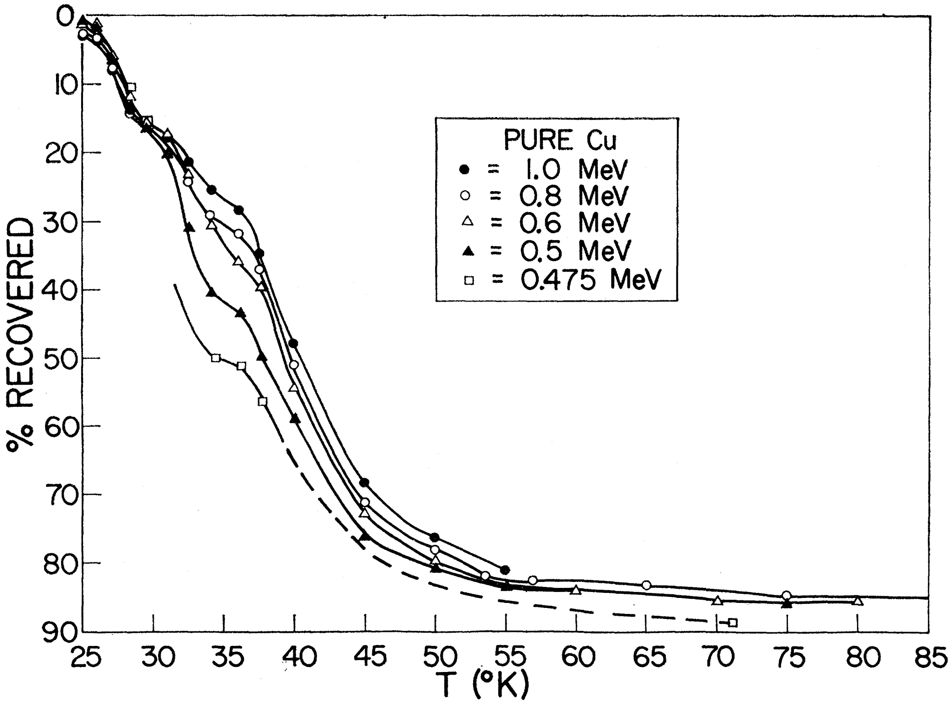

FIG. 4. Isochronal resistivity recovery spectra of pure copper following irradiation at 4.2°K with electrons of indicated incident energies.

transition between substage I_c and the higher temperature substage I_d is not ideally resolved, the actual data points in Fig. 1 are probably no better than ±1/2%. The point at 0.5 MeV for the 1.0 at. % alloy is not given since the resistivity was observed to increase in this case.

With the exception of the 1.0 at. % alloy, the main effects observed are as follows. The close-pair recovery stages are increasingly suppressed with increasing solute content at all energies. This suppression is still effective in all, except possibly the 0.03 at. % alloy, even down to electron energies of 0.5 MeV. As previously shown, the minimum threshold energy for copper is approximately 19 eV. This energy can only be imparted to a copper atom by an electron with a minimum energy of 0.4 MeV. Thus, suppression is effected even at relatively low electron energies.

While suppression is observed at all electron energies, the variation in amount of suppression is most prominent for energies below 0.6–0.7 MeV. At higher energies, up to 1.0 MeV at least, the amount of suppression remains essentially constant.

Examination of the suppression effects in each of the three close-pairs substages is limited by accuracy considerations. Suppression is effective in each of substages I_b and I_c and probably in I_a; the electron energy dependence of the suppression is similar in I_b and I_c.

Figure 3 shows the electron energy dependence of suppression of the entire stage I recovery. The data shown represent the extent of recovery as measured in the 45 to 55°K range. On identifying this with total stage I recovery, we are excluding the recovery in the temperature region around 60 to 65°K, which we identify as substage II_a.

To some extent, the data in Fig. 3 is very similar to that of Fig. 2. For example, the extent of suppression is concentration dependent in an analogous fashion and is quite constant for electron energies above 0.6 to 0.7 MeV, again. The only major difference appears to be that the electron energy dependence of the extent of suppression is less in the 0.5 to 0.7 MeV range in Fig. 3 than in Fig. 2. In fact, there appears to be no distinct energy dependence for the 0.3 at. % alloy. This is somewhat suspect, however. It is more likely that the data at 0.5 MeV should be some 10% lower but that resistivity increase effects, indicated for the 1.0 at. % alloy, are also present in the 0.3 at. % alloy.

Note that we have previously shown that total stage I recovery is almost entirely electron energy independent, up to at least 1 MeV, at approximately 85%. This also indicates that the extent of suppression is probably rapidly varying between 0.4 and 0.5 MeV.

Figures 4 through 6 show the results of an experiment in which pure copper and copper with 0.1 at. % Au, Ag, or Be were simultaneously irradiated. The recovery of resistivity in pure Cu, shown in Fig. 4, has been discussed in a previous publication. A comparison of Figs. 1 and 5 shows that 0.1 at. % Ag or Au affect the recovery very similarly. The close pair stages (below

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have been assumed to be due to recombination of interstitials with vacancies in which the recombination processes initially are fully correlated but become progressively uncorrelated as the remaining interstitials continue to migrate. For further discussion, see reference 1 and its references.

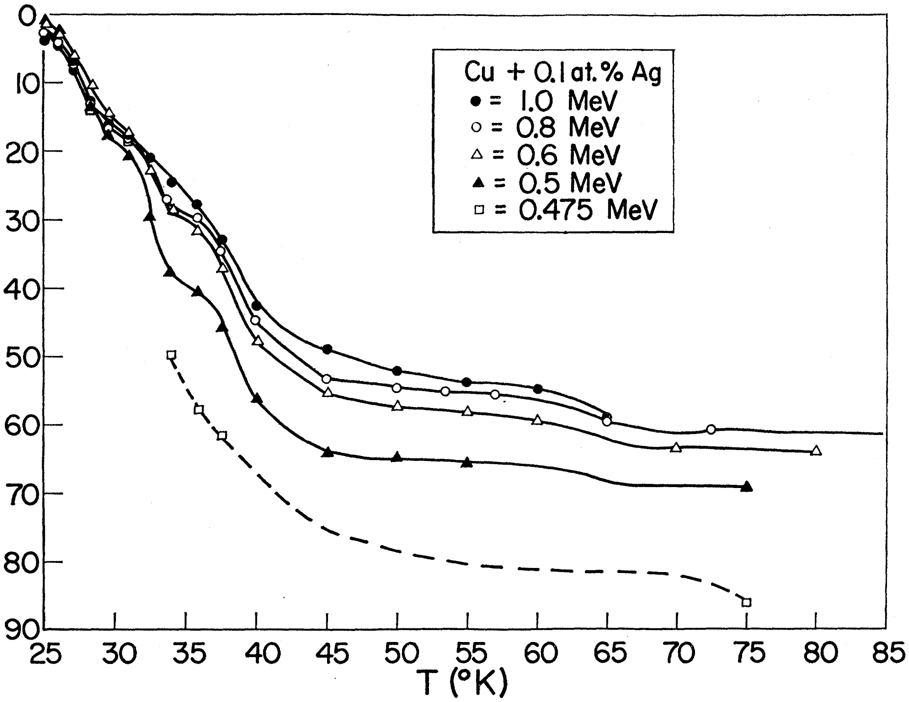

FIG. 5. Isochronal resistivity recovery spectra of Cu+0.1 at. % Ag following irradiation at 4.2°K with electrons of indicated incident energies.

35°K) are only slightly affected by this concentration of Ag or Au. However, the effects on substages I_d and I_e (35 to 55°K) are most noticeable. Again, it is seen that the effect of solute addition is most important at higher electron energies.

The effects of 0.1 at. % Be are quite different and complex. Here, it is noted that the close pair substages are affected by the Be addition, particularly I_c. The amount of suppression of entire stage I recovery is essentially independent of electron energy, in the energy range investigated, within experimental accuracy.

Some isothermal recovery data were also obtained. These data show that the monomolecular character of substage I_c is basically unaltered by the addition of 0.1 at. % Ag or Au. As expected, 0.1 at. % Be destroys this character. It is observed that the rate of recovery initially is somewhat more rapid in the more heavily gold-doped specimen than in pure copper.

DISCUSSION

The results presented above demonstrate that interaction generally occurs between solute atoms and the defects which migrate in stage I. We shall henceforth assume that an interstitial-type configuration migrates in stage I. All available data support this assumption.

With the choice of solute atoms explored here, it appears likely that the magnitude of the atomic size difference between the solute atom and the solvent (copper) atom is particularly important. This is also indicated by the results of Blewitt *et al.*[2] The source of this interaction remains largely unexplored.

Regardless of the detailed nature of the interstitial-solute interaction, the difference between the effect of Be in Cu and of Ag or Au in Cu indicates that interaction forces exist which extend over some appreciable distance, certainly in the case of Be. That this is true for Ag and Au is indicated further by the following attempt to account for the observed amount of suppression of recovery in gold-doped copper. Henceforth, the amount of suppression will be specified by a quantity S where

$$S=(R_C-R_A)/R_C, \tag{1}$$

in which R_C is the fraction of recovery in pure copper at a particular point in the annealing study and R_A is the equivalent fraction in the alloyed material.

Consider the recombination of the close pair configurations responsible for substages I_a, I_b, and I_c. We assume that the position of an interstitial with respect to its associated vacancy immediately following the radiation processes and prior to any thermal jump processes is not determined by the addition of solute atoms. This should be a reasonable approximation if the interstitial-vacancy separations are reasonably small, as is expected for close-pair configurations. We shall also assume that the solute atoms are randomly distributed and that solute atom clusters are absent or play no significant role.

If the interstitials were randomly distributed with respect to both vacancies and solute atoms and if these were equally effective in acting as sinks or traps, respectively, the probability of an interstitial being trapped by a solute atom rather than annihilated at a

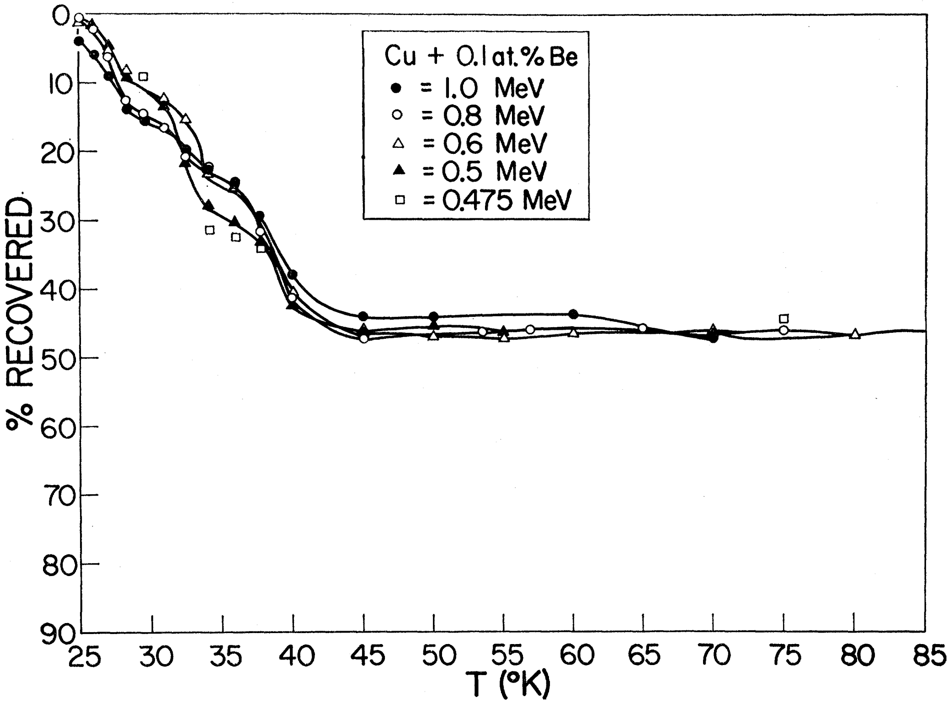

FIG. 6. Isochronal resistivity recovery spectra of Cu+0.1 at. % Be following irradiation at 4.2°K with electrons of indicated incident energies.

vacancy would be equal to the ratio of trapping sites to sink sites plus trapping sites. In order to account for the nonrandom character of interstitial-vacancy separation and inherently different tendencies for trapping or annihilating, we introduce the constants g_t and g_v, where the subscripts indicate trapping atoms or vacancies.

The relative probability of trapping is

$$P = g_t c_t / (g_v c_v + g_t c_t), \qquad (2)$$

where c_t and c_v are trap and vacancy concentrations. The probability of annihilation is $1-P$.

Table II presents data on recovery from Figs. 2 and 3. Since the fraction of recovery is quite independent of E for $E \geq 0.7$ MeV, typical data for this energy range were used. The points chosen for comparison with theory were taken at approximately 35 and 55°K. In this way, the data is broken up into two groups—a group representative of the close pair configurations of substages I_a, I_b, and I_c and a group presumably representative of the more distant configuration of substages I_d and I_e.

TABLE II. Parameters characterizing recovery of electrical resistivity following electron irradiation in copper plus several concentrations c of gold.

	Substage I_a, I_b, and I_e			Stage I	Substage I_d and I_e	
$c \times 10^4$	R	S	$g_t c_t / g_v c_v$	R	R	S
0	0.30	0	0	0.85	0.55	0
3	0.28	0.034–0.098	0.05	0.62	0.34	0.38
10	0.25	0.135–0.197	0.16	0.53	0.28	0.50
30	0.20	0.305–0.360	0.50	0.37	0.17	0.69

In order to compute P from the data, it is necessary to relate the recovery of electrical resistivity to defect decay and trapping. We shall assume that an interstitial continues to contribute fully to the resistivity when trapped in stage I. This is probably incorrect; however, the fact that well over half of the resistivity recovery in stage I is suppressed by a concentration of 10^{-2} gold atoms implies that the cross section for electron scattering by a free interstitial is not too different than that for a trapped interstitial. With this assumption, $P=S$.

The data in Table II, for the close-pair substages, are consistent within this model. Note particularly the values of $g_t c_t / g_v c_v$. These values imply that $g_t/g_v \approx 170$, if we set $c_v \approx 1$, recognizing that the basic process is close-pair recombination.

A similar conclusion may be reached through an analysis which emphasizes the small separation between an interstitial and a vacancy in a close-pair configuration. Here we consider each jump of the interstitial. The probability that an interstitial is trapped in its initial position is $P_1 \approx g c_t$ where the factor g is introduced to account for the extended interaction between interstitial and solute atoms. We anticipate that g is greater for Be than Ag or Au. The probability that the interstitial is not trapped in its initial position is $1-P_1$. If the interstitial is not trapped in its initial position, its first jump will take it to a new site which may serve as a trap. Henceforth, we only consider jumps to new sites (i.e., sites not previously visited).

The probability that an interstitial is not trapped in sampling $(i-1)$ sites is $(1-gc)^{i-1}$. Then the probability that the interstitial is trapped on sampling its ith new site is, approximately,

$$P_i = gc(1-gc)^{i-1}, \qquad (3)$$

and the probability that an interstitial is trapped on sampling n sites is

$$P = \sum_{i=1}^{n} P_i. \qquad (4)$$

Equation (4) has been applied to the data of Table II, with the assumption that all of the close pair configurations can be specified with a single average value of n. A reasonable fit is found with $n=2$ and $g \approx 70$. It appears from this result, as well as the previous analysis, that only a few jumps are made by the interstitial during close-pair recombination, which is as expected, and that the capture factor g is quite large.

Similar analyses have been attempted for the substages I_d and I_e recovery. As Table II shows, values of S (and, therefore, P) were derived by subtracting the close pair recovery from the total stage I recovery. A less satisfactory agreement between experiment and theory is found in this case. The results appear to be reasonable if the appropriate values of g_ic_i/g_vc_v are a factor of about 12 greater for $\mathrm{I}_d - \mathrm{I}_e$, as compared to the close-pair stages, and if the number of jumps in the more concentrated alloys is reduced somewhat beyond mere concentration effects. This latter is presumably an indication that the final position of an interstitial immediately following irradiation is determined to some extent by the impurity content. This conclusion implies that the number of sites an interstitial samples is now reasonably large, which is also the obvious explanation of the increase in the value of g_ic_i/g_vc_v. Thus, 24 appears to be a reasonable estimate of the number of sites samples by an interstitial, on the average, in substages I_d and I_e.

We next inquire as to the significance of our finding: $g \approx 70$. The simplest interpretation appears to be that a gold atom is surrounded by a "sphere" of interstitial sites in any of which an interstitial atom may be trapped. The factor of approximately 70 would represent the number of potential "trapping sites" at the surface of the "sphere." Such a "sphere" then must have a surface area at least equivalent to the planar area of 70 atom sites. From geometric considerations, we expect that the sphere will be of radius $r \gtrsim 3a_0$, where a_0 is the nearest neighbor distance in the face-centered cubic lattice.

It would be most desirable to make a unique identification of the various trapping sites and the interstitial-solute interaction energy for each such site. An attempt of this variety has been made by Hasiguti,[6] using a relationship developed by Eshelby[7] as a guide. Hasiguti suggests that there are four possible stable positions for an interstitial copper atom in the neighborhood of an oversized gold atom. Of the four, two positions are characterized by such small gold-interstitial interaction energies that it seems unlikely that they could be resolved. The most shallow of the remaining traps is characterized by an interaction energy of 0.03 eV, which implies an activation energy of 0.15 eV (the extra 0.12 eV represents the activation energy of a free interstitial atom). This seems appropriate for substage II_a, judging by the low temperature at which this substage occurs.

Hasiguti also calculates the interaction energy for the deeper trap to be 0.16 eV. This agrees sensibly with Martin's estimate of 0.20 eV binding energy for the interstitial which migrates in substage II_b. This leaves Martin's suggestion that release of interstitials from still deeper traps provided by pairs of gold atoms is responsible for substage II_c as most appropriate. If this assignment of traps is correct, the number of trapping sites around a gold atom is 32, somewhat less than our suggested figure of 70. This discrepancy could be due to our assumption that the interstitial retains its resistivity contribution on being trapped.

It appears then that over 30 potential trapping sites are associated with each gold (or silver) atom. This implies that these "trapping spheres" will overlap frequently in the 1.0 at. % alloy and, to a lesser extent, in the 0.3 at. % alloy. Without inquiring as to the details of process, it appears possible that the resistivity increases observed during annealing in the more concentrated Au-doped samples are related to this overlap.

The results of the addition of 0.1 at. % Be appear to be too complex to understand in detail at present. Nevertheless, it appears reasonable to deduce that the interaction of interstitials and Be atoms extends over considerably larger distances than the interaction between interstitials and Au or Ag atoms. This implies that the "trapping sphere" around Be atoms contains several hundred sites. It is little wonder, then, that the recovery of resistivity in 0.1 at. % Be is so effectively suppressed in stage I and that the subsequent stage II recovery is as complex as reported by Martin[3] and observed recently by us. Resistivity increases are observed in stage II in the case of the 0.1 at. % Be alloy.

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[6] R. R. Hasiguti, J. Phys. Soc. Japan **15**, 1807 (1960).

[7] J. D. Eshelby, Acta Met. **3**, 487 (1955).