

## Stage I Recovery Spectrum of Pure Copper Irradiated with Electrons over the Range 1.25 to 3.25 MeV\*

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(Received 8 August 1963)

A 99.999% pure copper specimen was irradiated at 20.4°K with 1.25-, 1.48-, 2.15-, 2.25-, and 3.25-MeV electrons. After irradiation at each energy the specimen was isochronally annealed to 60°K. Electrical resistivity at 20.4°K was the parameter measured. The results show that Stage I recovery is more complex than previously expected. The data show eight definite recovery substages and strongly indicates that possibly nine recovery substages exist in Stage I recovery. All substages were relabeled  $I_1$  through  $I_9$  for convenience. The new substages confirmed were labeled  $I_2$ ,  $I_7$ , and  $I_9$ . Substage  $I_2$  occurs at 22–23°K and represents 1.5–2% recovery. Substage  $I_7$  occurs at 45°K, is dose-dependent, and appears more clearly resolved after the higher energy irradiations. This substage,  $I_7$ , may correspond to the “bump” found at about 50°K by Nilan and Granato.  $I_9$  occurs at 53–59°K, represent 1% recovery and appears to be dose-dependent.  $I_9$  occurs near the temperature of the  $II_6$  substage reported by Sosin and Neely for doped copper. The shape of the isochronal derivative on the high-temperature side of  $I_8$  ( $I_D$  former notation) indicates that another substage,  $I_8$ , may be present. A similarity was noted between the recovery spectrum of gold and the new recovery spectrum of copper. A comparison with the results of others concerning the percent recovery associated with  $I_B$  and  $I_C$  (former notation) as a function of bombarding electron energy, supports the conclusion that not much change in population of  $I_B$  or  $I_C$  occurs beyond  $E=1.2$  MeV.

### INTRODUCTION

THE low-temperature recovery of physical properties of copper (known as Stage I) following irradiation at 20°K and lower, has been investigated by many. Electrons, deuterons, and neutrons have all been used to this end as the irradiating particle. The results of such investigations have shown that certain similarities and differences exist which have been attributed to the type of radiation used. The similarities consist in the most part of a number of well-defined recovery substages that are present in all the experiments. The amount of recovery taking place in a given substage, however, differs considerably for different experiments. Also, there exist some substages which do not clearly show in all of the experiments. These differences are thought to be largely due to the numbers of defects produced per particle-ion collision and to the distances separating defects. It has been fairly well established<sup>1–3</sup> that electrons with energy below about 1.4 MeV produce the simplest defects. Some of these are vacancy-interstitial pairs which recombine at characteristic temperature ranges up to about 34°K. Each substage temperature range is thought to be primarily a function of the distance of an interstitial from a vacancy from which it is removed by the order of a few interatomic distances. While this has been generally accepted as correct, still there are questions as

to the stable interstitial configuration, and the close pair configurations corresponding to the various substages.

At higher temperatures (34–65°K) free and correlated migration of interstitials is thought to occur. Corbett and Walker<sup>1,2</sup> have explored this possibility. Although the data had seemed to verify the existence of these interstitial motions, more recent work with deuterons<sup>4</sup> indicated that recovery in this temperature range is more complex. It is the purpose of this paper to provide additional experimental information toward answering some of the above questions. To this end, electrons with higher energy, up to 3.25 MeV, than those of others have been used to explore part of the range that should start showing transitions from low-energy electron-defect production. High doses for electrons were generally used to increase the resolving power. While this may also have the effect of suppressing certain substages,  $I_8$  ( $I_B$ ) for example, it was considered that it also might reveal some new substructure. This has been the case. Lower energy effects have been investigated by Corbett *et al.*<sup>1,2,5</sup> and by Sosin.<sup>3</sup>

### EXPERIMENTAL PROCEDURE

The sample was irradiated at 20.4°K using electrons supplied by a 0–5 MeV Van de Graaff. Liquid hydrogen was used as a refrigerant. Beam currents of more than  $6 \mu\text{A}/\text{cm}^2$  could easily be used without raising the sample temperature.

The parameter used to detect the defects produced by the bombarding electrons was the low-temperature electrical resistivity. To this end, a Rubicon 6-dial thermofree potentiometer was employed to measure the voltage drop across the sample with a

\* This paper is based on the Ph.D. thesis research of J. A. Tesk. Supported jointly by the Advanced Research Projects Agency of the U. S. Department of Defense, through the Northwestern University Materials Research Center, and by the U. S. Atomic Energy Commission.

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<sup>1</sup> J. W. Corbett, R. B. Smith, and R. M. Walker, *Phys. Rev.* **114**, 1452 (1959).

<sup>2</sup> J. W. Corbett, R. B. Smith, and R. M. Walker, *Phys. Rev.* **114**, 1460 (1959).

<sup>3</sup> A. Sosin, *Phys. Rev.* **126**, 1698 (1962).

<sup>4</sup> A. Granato and T. Nilan, *Phys. Rev. Letters* **6**, 171 (1961).

<sup>5</sup> J. W. Corbett and R. M. Walker, *Phys. Rev.* **115**, 67 (1959).

TABLE I. Pertinent irradiation and annealing information.

Irradiation number in order performed	1	2	3	4	5	6	7	8
Electron energy at midpoint of specimen (MeV)	1.25	1.25	2.25	2.25	3.25	3.25	1.41	2.15
Radiation induced resistivity at 20.4°K $\Delta\rho$ ( $10^{10}$ $\Omega$ -cm)	30.0	40.5	25.3	39.8	43.4	65.4	156.0	12.6
Isochronal annealing temperature intervals (°K)	~3	~3	1.5 and 2.0	1.5	1.5	1.5	1.5	0.75
Annealing time (minutes)	10	10	10	10	10	10	10	10
Temperature annealed to (°K)	65	65	65.5	63.5	62.0	54.5	59	26.75

fixed current of 0.25000 A passing through the sample. The current was controlled to at least  $\pm 0.00001$  A by a servo-mechanism. A Leeds and Northrup photoelectric galvanometer amplified the signals fed into a standard coil-suspension-type galvanometer. Extreme care was taken in thermal and electrical shielding and the making of necessary potential lead contacts. This enabled resistivity to be determined to the nearest  $2 \times 10^{-8}$   $\Omega$ , with a corresponding uncertainty in resistivity of  $\sim 1 \times 10^{-12}$   $\Omega$ -cm. High defect concentrations were generally produced, so that mean deviations in the measured radiation induced resistivities were  $\pm 0.10$ – $0.15\%$ , and for the highest dose experiment (No. 7)  $\pm 0.05\%$ .

The sample and sample holder were the same as that used by R. M. Walker *et al.*<sup>1,2</sup> The sample was 0.0032 cm thick and 99.999% pure, zone-refined copper.

Essentially, the cryostat was Corbett's and Walker's<sup>1,2,6</sup> original except for a few modifications. A major modification was necessary to convert the cryostat for use with a horizontal rather than a vertical electron beam. An important modification resulted in better temperature stability from 20.4°K on up. This modification consisted, first of all, in enlarging a section of the entrant tube leading to the sample holder from the liquid-hydrogen reservoir. An extra low-power heating coil was wrapped around this section. This combination resulted in an arrangement whereby hydrogen could be evaporated, slightly warmed, and passed over the sample. It minimized the danger of sudden temperature drop resulting from the liquid's being suddenly pulled over the sample due to a slight variation of pressure in the hydrogen flow system. The larger mid-section of the entrant tube acted as a sort of "ballast tank."

Temperature was manually controlled by combinations of heat supplied to one or more of three heaters and/or adjusting the flow of evaporated hydrogen gas in the system over the sample. Maximum temperature fluctuation about the average generally was  $< \pm 0.2\text{K}^\circ$ , just above 20.4°K,  $\leq \pm 0.1\text{K}^\circ$  at 25°K and continually decreased to  $\leq 0.05\text{K}^\circ$  at 40°K and above. Temperature was measured by means of the voltage drop across

a calibrated copper control sample through which the 0.25000 A were also passed. During the irradiation and the subsequent anneals, the temperature was continuously monitored and displayed on a chart recorder. The irradiation temperature was kept at 20.4°K by a steady flow of liquid hydrogen over the sample.

Table I shows additional information pertinent to the experimental procedure.

After the completion of each of the isochronal annealing experiments, the specimen was annealed in vacuum at either 100°C for  $1\frac{1}{2}$  h or room temperature for one day. The total unrecovered radiation-induced resistivity from all the experiments was  $\sim 1\%$  of the bulk resistivity before irradiation. No effect on the results of the annealing studies was observed as a result of this gradual accumulation. For example, all specimens had attained 84% recovery by 60°K.

## EXPERIMENTAL RESULTS

The isochronal annealing data revealed eight definite recovery substages and strongly suggests a ninth substage within Stage I recovery in copper. For convenience, all substages have been relabeled with an  $I_1$  to  $I_9$  sequence.  $I_1$  was not observed; it is  $I_A$  on the former notation and occurs below the irradiation temperature. Corresponding notation for previously identified substages is  $I_3$  ( $I_B$ ),  $I_4$  ( $I_C$ ),  $I_5$  ( $I_D$ ), and  $I_8$  ( $I_E$ ). Figure 1 shows the isochronal annealing derivatives along with the labeling of substages. Figure 2 shows pronounced steps of the isochronal recovery. The first new substage occurred between 22–23°K. This stage has been called  $I_2$ .  $I_2$  was reproduced in all experiments. Its detection was made possible because of the high dose of the experiments and improved temperature control between 20.4 and 25°K for the particular apparatus used.<sup>1</sup> This enhanced the relative sensitivity of the experiments. Others may not have detected this substage by resistivity since the stage represents only about 1.5–2% recovery, and as mentioned, considerable effort was made in order to increase resolution.

Some additional structure is evident on the high-temperature side of  $I_5$  ( $I_D$ ) at 45°K. A definite annealing peak occurs at 45°K after two 3.25-MeV irradiations. This peak has been called  $I_7$ . The experiment with the higher dose shows some merging of this

<sup>6</sup> J. W. Corbett, J. M. Denney, M. D. Fiske, and R. M. Walker, *Phys. Rev.* **108**, 954 (1957).

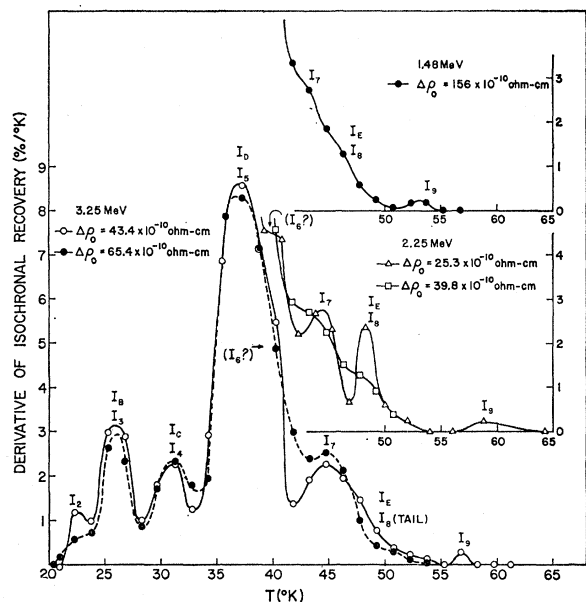


FIG. 1. Negative of the numerical derivative of isochronal recovery curves of all irradiations versus mean of annealing temperature in °K. Derivative computed from:

$$\frac{(\Delta\rho/\Delta\rho_0)_{T_1} - (\Delta\rho/\Delta\rho_0)_{T_2}}{(T_1 - T_2)} \sim \frac{d(\Delta\rho/\Delta\rho_0)}{dT}$$

For the 1.48- and 2.25-MeV curves only the portions above about 37°K are shown since the lower temperature portions are essentially the same as that shown for 3.25 MeV.

peak with  $I_5$  ( $I_D$ ). Peak  $I_7$  shows again at 45°K for the lower dose of the two 2.25-MeV irradiations. The higher dose of the 2.25-MeV irradiation appears to have merged with  $I_5$  ( $I_D$ ), to produce a ballooning out of the recovery spectrum toward 45°K. After a very high dose experiment at 1.48 MeV, there is only slight

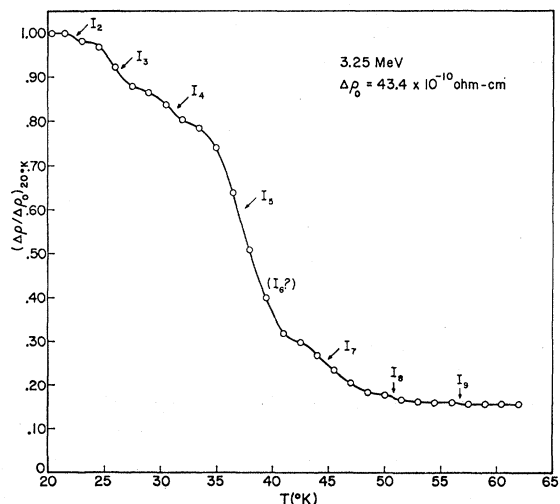


FIG. 2. Fractional recovery remaining after 10-min anneals versus annealing temperature in °K. Recovery substages are shown.

but definite evidence of structure on the high side of  $I_5$  ( $I_D$ ).

It should be noted that most of these experiments were done with concentrations high enough to suppress  $I_8$  ( $I_E$ ), and in the one exception,  $I_8$  ( $I_E$ ), does clearly show distinct from  $I_7$ . Also, a tailing off of  $I_7$  to high temperatures is taken as the small amount of  $I_8$  ( $I_E$ ) which does show. Therefore, it is felt that a new peak is definitely being observed, and not just  $I_8$  ( $I_E$ ) at lower temperature.

Another small stage in the recovery spectrum is observed at 57–59°K for all experiments, except the high dose, 1.48-MeV irradiation, after which the peak had shifted to 53°K. This stage represents about 1% recovery. This stage could actually be the start of  $II_a$  recovery reported by Sosin and Neely,<sup>7</sup> after their impurity doping experiments, but for a high-purity copper specimen.

The shape of the  $I_5$  ( $I_D$ ) on the high-temperature side indicates that another substage,  $I_6$ , may be present between  $I_5$  and  $I_7$ . This has been indicated on the curves shown in Fig. 1.

A comparison of the percent recovery associated with stages  $I_B$  and  $I_C$  (former notation) as a function of the electron energy, reveals and substantiates the trends indicated by others.<sup>3,5,8</sup> Only a small but definite decrease in population of  $I_B$  and  $I_C$  occurs beyond  $E=1.2$  MeV. Table II shows the experimental results and some of those of others.<sup>5,8</sup>

Damage production rates were also measured over the range 1.1 to 2.7 MeV and should be reported in the future.

## DISCUSSION

The results indicate that the recovery may be more complex than previously indicated by others.<sup>1-3,5,8</sup>

As far as we know, stage  $I_2$  has not been reported by others using electrical resistivity. Nilan and Granato,<sup>4</sup> measuring stored energy, have reported some annealing on the low-temperature side of  $I_B$ , at a temperature slightly higher (by  $\sim 2^\circ\text{K}$ ) than our  $I_2$ . This difference in temperature could be attributed to the differences in annealing times at temperature, their times being shorter. It is felt that this annealing around 22°K in both experiments is due to the same process. E. Ichinohe<sup>9</sup> has since observed  $I_2$  independently measuring resistivity after irradiation at about 15°K, and using different apparatus. Therefore, this new stage in the annealing spectrum has been definitely established.

Stage  $I_7$  offers some difficulty at first, due to the fact that it did not always appear as a separate, well-defined annealing peak, and has not been reported by others measuring resistivity. A closer look at the results indicate that  $I_7$  is energy and concentration sensitive.

<sup>7</sup> A. Sosin and H. H. Neely, Phys. Rev. **127**, 1465 (1962).

<sup>8</sup> R. L. Chaplin and P. E. Shearin, Phys. Rev. **124**, 1061 (1961).

<sup>9</sup> E. Ichinohe, Northwestern University (experiments now in progress).

TABLE II. Percent recovery associated with substages  $I_B$  and  $I_C$  (former notation) as a function of energy for electron energies between 1.2 and 3.3 MeV.

Electron energy MeV	1.25 Present experiment	1.40 Corbett and Walker <i>et al.</i> <sup>5</sup>	1.48 Present experiment	2.0 Chaplin and Shearin <sup>9</sup>	2.25 Present experiment	3.25 Present experiment
Recovery stage $I_2+I_3$ ( $I_B$ ) <sup>a</sup>	14±1.7	13.1%	13.5±0.5	12.0	12.0±1.5	11.7±0.8
$I_C$	11±1.0	10.0	9.0±0.5	9.3	8.7±0.8	8.0±0.5

<sup>a</sup>  $I_2+I_3$  are taken =  $I_B$  for comparison, since annealing taking place in  $I_2$  was formerly attributed to  $I_B$ .

Higher energy experiments tend to delineate it, higher dose tends to obscure it. This observation is not contradicted by the results of others.<sup>1-3</sup> Their experiments were with lower energy, which would have made it more difficult to reveal  $I_7$ . A low dose with low energy could conceivably reveal  $I_7$ , but then the percent resolving power is decreased as a result of the low dose. In the data of Corbett and Walker *et al.*,<sup>1,2</sup> there is some indication of a process around 45°K, uncertain, however, possibly because of the problem of resolution. Nilan and Granato<sup>4</sup> observe a bump on the high-temperature side of  $I_5$  ( $I_D$ ) at ~50°K. If the temperature of  $I_5$  ( $I_D$ ), 37°K, in this experiment were normalized to match  $I_D$ , 42°K, of Nilan and Granato,<sup>3</sup> then the peak found at 45°K,  $I_7$ , would occur at 51°K on the normalized temperature scale, hence coincide with their "bump" at ~50°K. Their 10-MeV deuterons could be expected to give some of the effects of electron irradiations. Considering their bump to be  $I_7$ , then it would not seem unreasonable according to the energy-dose effect that the high energy of their incident particles helped them to observe  $I_7$  while the high concentration tended to obscure it, resulting in a bump rather than a well-defined peak. The concentration effect is in evidence from their higher dose experiment, i.e.,  $I_7$  has merged more with  $I_D$ .

Stage  $I_9$  occurs in the same temperature range as Sosin's and Neely's<sup>7</sup>  $II_a$ . The low amount of recovery associated with this stage, ~1%, would at first glance make it seem quite likely that this is  $II_a$  for a high-purity specimen, i.e., only a small amount of impurity trapping of interstitials. The results do not indicate that  $I_9$  is that simple;  $I_9$  occurs at a lower temperature, 53°K, for the high dose, 1.48-MeV irradiation. After the other irradiations (all at a lower dose than the 1.48-MeV run) the recovery temperature is 57-59°K. The effect could be due to energy or concentration or both. Unfortunately, no direct comparison of concentration dependence of  $I_9$  at one energy is available. (The refrigerant was used up before  $I_9$  could be reached during one of the 2.25-MeV runs. Three runs do reliably reproduce  $I_9$ .) However, it can be seen that there is a consistent shift toward lower temperature with increasing concentration, while no systematic dependence on energy can be observed. If one assumed that the recovery temperature was only concentration-dependent

and involved a recombination process, then a simple calculation based on the shift of temperature with concentration, assuming an activation energy of 0.10-0.12 eV,<sup>2</sup> would yield an apparent order of reaction of about 1.5. If this stage were only due to release of interstitials from traps, then no energy or concentration dependence would be expected, the temperature depending only on the binding energy of the trap. Therefore, it actually may be that  $I_9$  is not the same as  $II_a$ ,<sup>7</sup> but no conclusion can be arrived at based on existing data.

The shape of the isochronal derivative between  $I_5$  and  $I_7$  indicates that additional, but unresolved, structure may be present. Nilan and Granato<sup>4</sup> observed "fine structure" on the high-temperature side of their  $I_D$  ( $I_5$ ), and that again on a temperature scale normalized to their  $I_D$ , the suspected temperature of  $I_6$  coincides with their fine structure, i.e., 43-44°K.

It is expected that these results may have important bearing on determining whether the split or body-centered interstitial is stable in copper. The appearance of additional substructure would appear to favor the split interstitial, since the split interstitial has lower symmetry than the body-centered interstitial.

It is interesting to compare the post low-temperature electron-irradiation recovery spectra of copper and gold as shown in Table III. Most of the data on the gold is by Ward and Kauffman<sup>10</sup> or by Bauer *et al.*<sup>11</sup> Some of Herschbach's<sup>12</sup> data are included since recovery following deuteron irradiation should be somewhat similar to that following electron irradiation, especially as far as close pair recovery processes are concerned. In Table III it is immediately seen that there are nine recovery substages in the spectra of both copper and gold. If the highest peak of copper,  $I_5$ , is considered to correspond to the most prominent peak in gold (18°K), then in each case the peak is followed in temperature by four successively smaller peaks. More important, is the fact that the highest peak in each case is preceded in temperature by four peaks. Further, the ratios of the peak temperatures, copper to gold, are essentially the same for peaks  $I_3$ ,  $I_4$ , and  $I_5$ , i.e., 2.2. No isochronal peaks

<sup>10</sup> J. B. Ward and J. W. Kauffman, Phys. Rev. **123**, 90 (1961).

<sup>11</sup> W. Bauer, J. W. DeFord, J. S. Koehler, and J. W. Kauffman, Phys. Rev. **128**, 1497 (1962).

<sup>12</sup> K. Herschbach, Phys. Rev. **130**, 554 (1963).

TABLE III. Recovery data of electron-irradiated copper and gold. Data are obtained from experiments using 2.25–3.25-MeV electrons. Substages are labeled in the order of their occurrence with increasing temperature. Isochronal data give temperatures of recovery for corresponding activation energies. In gold, only activation energy of peaks in activation energy spectrum are available for first two substages. The first five substages are expected to correspond to close pair recovery processes.

Recovery substage		I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>	I <sub>4</sub>	I <sub>5</sub>	I <sub>6</sub>	I <sub>7</sub>	I <sub>8</sub>	I <sub>9</sub>
Approximate recovery temperature °K (from isochronal experiments)	Cu	16 <sup>a</sup>	22.5 <sup>b</sup>	26 <sup>ab</sup>	31.5 <sup>ab</sup>	37 <sup>ab</sup>	39 <sup>b</sup>	45 <sup>b</sup>	48 <sup>ab</sup>	53 <sup>b</sup>
	Au			12 <sup>c</sup>	14.5 <sup>cd</sup>	18 <sup>ode</sup>	23 <sup>de</sup>	28 <sup>ode</sup>	37 <sup>d</sup>	42 <sup>de</sup>
Ratio substage temperatures copper to gold				2.2	2.2	2.1	1.7	1.6	1.3	1.3
Substage activation energy eV	Cu <sub>a</sub>	0.050	0.068 <sup>f</sup>	0.085	0.095	0.12				
	Au <sub>de</sub>	±0.010	±0.010	±0.010	±0.010	±0.005				
Substage activation energy, eV, calculated from Cu and temperature ratio Cu to Au=2.2	Au	0.023	0.031	0.039	0.043	0.055				
Ratio I <sub>n</sub> /I <sub>5</sub>	Cu <sub>b</sub>					1	0.50	0.33	0.26	0.02
Peak height to prominent I <sub>5</sub> n≥5	Au <sub>d</sub>					1	0.37	0.19	0.16	0.13

<sup>a</sup> From Refs. 1, 2.  
<sup>c</sup> From Ref. 12.

<sup>b</sup> From present experiment.

<sup>e</sup> From Ref. 13.

<sup>d</sup> From Ref. 11.

<sup>f</sup> Estimated from activation energy of I<sub>4</sub> and temperatures of substages I<sub>2</sub> and I<sub>4</sub>.

corresponding to I<sub>1</sub> and I<sub>2</sub> were resolved in gold, however, the activation energy spectrum of Bauer *et al.*<sup>11</sup> shows five substages up to and including the most prominent peak in gold. Since I<sub>3</sub> and I<sub>4</sub>, and likely I<sub>5</sub>, recover according to first-order kinetics in copper, the constant ratio would seem to imply that there are corresponding substages in gold which recover the same way. If this is true, then based on this ratio and the activation energies reported by Corbett *et al.*,<sup>1,2</sup> for the first substages in copper, we should be able to calculate the activation energies for the first five substages in gold and compare these with those published by Ward and Kauffman<sup>10</sup> and by Bauer *et al.*<sup>11</sup> In copper, the activation energy of I<sub>2</sub>, which has not been determined, was estimated from that of I<sub>4</sub>,  $\epsilon(I_2) = [T_2/T_4]\epsilon(I_4)$ .  $\epsilon$  = the activation energy and  $T$  = the absolute temperature. The average values of the activation energies in copper were used, and the computed values of activation energy in gold based on the aforementioned ratio are in excellent agreement with those reported by others. The success of the comparison indicates that gold and copper undergo the same close-pair recovery processes and that the smaller amount of close-pair recovery in gold is the result of stronger focusing as suggested by Silsbee,<sup>13</sup> and possibly stronger  $\langle 100 \rangle$  focusing by the surrounding ions, found by Gibson *et al.*,<sup>14</sup> caused by the larger ratio of ionic radius to the lattice parameter for gold, hence, lower populations of close pairs. Bauer *et al.*<sup>11</sup> have suggested that the smaller amount of low-temperature recovery is due to stronger focusing. Recovery at higher temperatures than that of I<sub>5</sub> also appears rather similar, although differences again are expected in the interactions involved, the gold interstitial exerting a longer ranged interaction as suggested by Ward and Kauffman.<sup>10</sup>

In the comparison in Table III we have omitted a substage reported at 21°K by Bauer *et al.*<sup>12</sup> for the following reasons. They had only one run, reported that they had experimental difficulties at this temperature, and the two experiments by Ward and Kauffman,<sup>10</sup> using smaller temperature intervals, did not resolve a 21°K substage. Although the 21°K substage may exist, we have preferred to leave it out of the comparison until further work confirms its existence. Substage I<sub>6</sub> of the copper has been left in since the work of Nilan and Granato<sup>4</sup> supports the existence of the I<sub>6</sub> substage in copper as previously discussed.

#### SUMMARY

Stage I recovery of copper, following electron irradiation in the range 1.48 to 3.25 MeV, has been observed to be highly complex. Three new substages (I<sub>2</sub>, I<sub>7</sub>, I<sub>9</sub>) have been detected and a fourth (I<sub>6</sub>) has been indicated by the data. The total number of observed substages is therefore raised to eight or nine. Substage I<sub>2</sub> occurs at 22–23°K and represents 1.5–2% recovery. I<sub>7</sub> occurs around 45°K and tends to merge with I<sub>5</sub> (I<sub>D</sub>) at higher concentrations. It was shown that I<sub>7</sub> would correspond with the “bump” found by Nilan and Granato<sup>3</sup> at ~50°K. I<sub>7</sub> is more clearly observed at higher energy. Substage I<sub>9</sub> occurs between 53–59°K, represents ~1% recovery, and appears to shift from the 59 to 53°K with increasing defect concentration. I<sub>9</sub> may be substage II<sub>a</sub> reported by Sosin and Neely,<sup>5</sup> however, the concentration dependence of I<sub>9</sub> indicates that it should not be due to simple breaking away of interstitials from traps. The slight bowing out of peak I<sub>5</sub> between I<sub>5</sub> and I<sub>7</sub> indicates that another substage, I<sub>6</sub>, could be present. This would likely be the extra “fine structure” found by Nilan and Granato<sup>3</sup> on the high-temperature side of I<sub>5</sub> (I<sub>D</sub>).

The present recovery in I<sub>B</sub> and I<sub>C</sub> (former notation)

<sup>13</sup> R. H. Silsbee, J. Appl. Phys. **28**, 1246 (1957).

<sup>14</sup> J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).

as a function of energy was compared with the results of others. The small trend toward lower populations of defects in  $I_B$  and  $I_C$  with increasing electron energy is supported. It may be necessary to review the significance of the change at lower energy<sup>3,5</sup> since the present experiment has shown that  $I_B$  actually consists of two substages,  $I_2$  and  $I_3$ .

Further work is required to relate the eight or nine substages to the corresponding detailed recombination process together with the determination of the stable interstitial configuration in copper. Such work is now in progress.

A comparison of the new recovery spectrum of copper with that of gold indicates that the first few substages of recovery are due to the same processes,

hence, many of the same types of defects are produced, only in different concentrations in the two metals.

#### ACKNOWLEDGMENTS

The authors wish to thank Dr. R. M. Walker for use of his specimens and cryostat (which was modified) and for the generous amount of his time spent in discussions and in suggestions. Mrs. E. L. Fontanella of GE Labs is thanked for her suggestions on some experimental techniques. The conscientious help of R. C. Erwood, L. A. Watson, J. Scott-Monck, and K. O. Koestler is gratefully acknowledged.

Dr. E. N. Strait and H. H. Hagelauer are thanked for their cooperation concerning the operations at the Northwestern Nuclear Physics Research Laboratory.

### Experiments on Stage III Annealing in the Noble Metals\*

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(Received 26 August 1963)

High purity copper, silver, and gold specimens have been irradiated with 10-MeV protons near 80°K. An integrated flux of  $1 \times 10^{17}$   $p/cm^2$  produced a resistivity increase of  $3.3 \times 10^{-8}$   $\Omega\text{-cm}$  in copper,  $7.4 \times 10^{-8}$   $\Omega\text{-cm}$  in silver, and  $16.6 \times 10^{-8}$   $\Omega\text{-cm}$  in gold. The specimens were isothermally annealed in steps of 20°K for 64 min at each temperature from 143 to 363°K. The recovery in stage III follows second-order kinetics with an activation energy of  $0.71 \pm 0.04$  eV for copper,  $0.67 \pm 0.03$  eV for silver, and  $0.80 \pm 0.04$  eV for gold. Distribution curves of the fractional concentration of defects annealing with a given activation energy have been calculated. In the case of copper and silver they show a complex structure followed by a large broad maximum at 0.71 eV for copper and 0.67 eV for silver. In gold there is only one large peak at 0.80 eV. The relationship of these results to the various models is discussed.

#### I. INTRODUCTION

THE recovery of the electrical resistivity change which occurs in irradiated noble metals in the range from 200 to 300°K (stage III) has been studied in a number of experiments, but only few kinetic measurements have been made. Overhauser<sup>1</sup> measured the isothermal annealing of 99.99% pure copper irradiated with 12-MeV deuterons at 100°K. He observed a recovery process that had an activation energy of 0.68 eV and that obeyed a chemical rate equation of 2.5 order. Meechan and Brinkman<sup>2</sup> and Meechan, Sosin, and Brinkman<sup>3</sup> irradiated high purity copper with 1.25-MeV electrons at 80°K and investigated the recovery of the electrical resistivity change upon annealing. They found a second-order process

with an activation energy of 0.60 eV. Kauffman<sup>4</sup> reports a recovery process with an activation energy of  $0.72 \pm 0.05$  eV in gold after electron irradiation near 100°K.

Various models have been proposed to explain the recovery in stage III, but it is still uncertain what the nature of this recovery process is. Following are the possibilities which have been suggested: migration of a vacancy; migration of a divacancy; migration of a second kind of interstitial; migration of a diinterstitial; and breakup of interstitial complexes.

In the case of gold the energy of motion of a single vacancy is known to be<sup>5</sup>  $0.82 \pm 0.05$  eV and that of a divacancy  $0.64 \pm 0.04$  eV,<sup>6</sup> and in the case of silver the energy of motion of a single vacancy  $0.83 \pm 0.05$  eV,<sup>7</sup> and that of a divacancy  $0.57 \pm 0.03$  eV.<sup>7</sup>

The present research was carried out with the hope that it might clarify this situation by comparing the

\* Research supported by the United States Atomic Energy Commission.

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