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Isochronal annealing of proton- or α-particle-irradiated Cu_3Au at low temperatures

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Isochronal annealing experiments have been made below 90 K by electrical resistivity measurement on ordered and disordered Cu_3Au, and Cu irradiated with ~4.7-MeV protons or ~17.8-MeV α particles below 30 K. In the ordered Cu_3Au, several annealing stages have been observed; a small reverse annealing stage below 40 K, small recovery stage(s) between 40 and 52 K, and a large one around 70 K. The small stage(s) between 40 and 52 K and the large one are interpreted to be due to the close-pair recovery and the long-range migration of Cu interstitials, respectively. In the α-particle irradiation a large reverse annealing stage has been observed above 30 K with increasing irradiation dose. In the disordered Cu_3Au the recovery is small (~10%) and almost completed at 60 K.

I. INTRODUCTION

Irradiation effects in Cu_3Au have been investigated since the beginning of radiation-effects research.[1-5] Such an ordered alloy is a most promising type of system to study replacement collision in damage production and migration of vacancies, because their effects are observed as a large change in the ordered state. Therefore, the detailed study of ordered alloys will give important information on the damage-production process and the behavior of defects.

For the study of the damage-production process, experiments around liquid-helium temperature are highly required. Several experiments have been performed on the ordered Cu_3Au. Takamura and Okuda[6] and Alamo, Desarmot, and Dirand[7] have made electrical resistivity measurements under fast-neutron irradiation. They measured damage-production rates and deduced the number of replacements per Frenkel pair to be about 50 and 70, respectively. In previous papers we also reported the damage-production rates obtained by electrical resistivity measurements under ion irradiation with protons, α particles, and C ions of various energies.[8-10] The number of replacements per Frenkel pair was estimated to be about 27. On the other hand, significant radiation disordering was not observed in the experiments with 1- and 1.5-MeV electrons made by Gilbert, Herman, and Damask.[11] The average displacement threshold energies were estimated to be about 24 eV for Cu and about 18 eV for Au in the irradiation experiments with 0.4–2.5-MeV electrons by Alamo, de Novion, Lesueur, and Dirand.[12] Thereafter the minimum displacement threshold energy for Cu, $E_{d,\min}^{\mathrm{Cu}}$, was determined to be 18 eV.[13] Hameed, Smallman, and Loretto estimated $E_{d,\min}^{\mathrm{Cu}}$ to be about 14 eV from the determination of a threshold voltage for disordering of an ordered Cu_3Au under electron irradiation at 160 K in an electron microscope.[14] To directly observe the damage structures electron microscopic observation has been made of the ordered Cu_3Au irradiated with Cu^+ ions[15,16] or protons[16] or neutrons[16,17] at room temperature, and the size distributions of disordered zones have been obtained.

For understanding of damage structures and behavior of irradiation-induced defects, annealing experiments at low temperatures are necessary. The isochronal annealing experiments below 150 K performed by electrical resistivity measurements on neutron-irradiated ordered Cu_3Au revealed the presence of only one distinct stage around 100 K (Ref. 6) or two stages around 40 and 70 K,[7] while those on electron-irradiated Cu_3Au showed only one stage around 75 K (Ref. 11) or two stages around 35 and 70 K.[13] There has been no experiment on ion irradiation. In the present research, proton and α-particle irradiations have been carried out using a cyclotron on ordered and disordered Cu_3Au below 30 K and isochronal annealing experiments have been made up to 100 K. These results are reported together with the results on Cu.

II. EXPERIMENTAL PROCEDURE

A. Specimen preparation

Cu foils of 99.996% purity 50 μm in thickness (supplied by MRC) were cut into a bridgelike shape 1 mm wide by 15 mm long for the electrical resistivity measurement. After chemical polishing they were annealed in an evacuated quartz capsule at 1173 K for 0.5 h. Their average thickness were 20–30 μm.

Cu_3Au alloys were prepared by melting Cu and Au of 99.999% purity in a quartz capsule. The Au concentration of this alloy was 25.8 at. %. The samples were processed to foils 30 μm in thickness by repeating several times cold rolling and annealing. These foils were cut into a bridgelike shape as in the case of Cu and annealed at 1073 K for 0.5 h. Heat treatment for ordering follows

Cook and Cushing;[4] annealing for 0.5 h at 1073 K in a vacuum, furnace cooling to 623 K, 6 h at 623 K, 16 h at 613 K, 4 h at 603 K, 4 h at 593 K, 16 h at 573 K, and furnace cooling to room temperature. Their electrical resistivities were about 5.8 $\mu\Omega$ cm at room temperature and 2.3–2.8 $\mu\Omega$ cm at liquid-helium temperature. Disordered specimens were prepared as follows; annealing for 0.5 h at 1073 K in a vacuum, furnace cooling to room temperature, 1 h at 773 K in an evacuated Pyrex glass capsule, and quenching in silicone oil. Their electrical resistivity was about 12 $\mu\Omega$ cm at room temperature and 10 $\mu\Omega$ cm at liquid-helium temperature.

B. Irradiation

Irradiation was carried out by using a cyclotron under the condition for incident ions to penetrate the specimens. A specimen holder was made of a mica plate stuck on a 1-mm-thick Cu plate with GE7031 varnish. In order to minimize the increase of specimen temperature by beam heating during irradiation a square hole 5 mm wide by 8 mm long was made at the center of this holder. The specimens were set across this hole by sticking both their ends with varnish on a mica plate so that an ion beam outgoing from the specimens passes through this hole.

For electrical resistivity measurement current leads and potential leads (Cu wire with a 0.2-mm diameter) were soldered to both the ends and outside arms on either side of the bridge-shaped specimen, respectively. The specimen holder was set on a copper block which was connected to a liquid-helium reservoir in a cryostat with a stainless pipe. A needle valve was equipped at a connecting part between the pipe and the reservoir. Manganin heater wire was wound around the copper block. Temperature control was performed by changing heater current and the flow rate of liquid helium through the needle valve. At the beam inlet of the cryostat, a 40-μm-thick Al foil, in some cases a 150-μm-thick Al foil, was placed to isolate the cryostat from a vacuum system of the cyclotron. Incident beam which had penetrated the Al foil was collimated by two slits in the cryostat and irradiated the specimens. An irradiation area was defined by a slit to be about 7 mm wide by 11 mm long. In most cases irradiation was performed with 6-MeV protons or 23-MeV α particles. Ranges of these ions are large enough for the incident ions to penetrate the specimens. Taking account of energy loss in the Al foil and the specimens the average energy in the specimens was about 4.7 MeV for protons and about 17.8 MeV for α particles. Beam current was between 30 and 50 nA. During irradiation, temperature was kept below 30 K. The isochronal annealing experiment of electrical resistivity was performed up to 100 K in 5-min pulses. Resistivity was measured at liquid-helium temperature. Temperature measurement was made with a Cu-versus-Au–2.1 at. % Co thermocouple.

III. EXPERIMENTAL RESULTS

Irradiation conditions on various specimens are listed in Table I. Irradiation dose was chosen to obtain approximately the same amount of irradiation-induced resistivity increase in both proton and α-particle irradiations, and varied by a factor of about 3.

A. Cu

Figure 1 shows the results of isochronal annealing for 5-min pulses on Cu specimens irradiated below 15 K with 4.8-MeV protons and 17.7-MeV α particles. Normalization of the fractional resistivity change $\Delta\rho/\Delta\rho_0$ (with $\Delta\rho$ the resistivity increase unrecovered by the annealing) is

TABLE I. List of specimens and properties. Included is the energy of a beam after passing through the Al foil placed at the beam inlet of the cryostat, and $\langle E \rangle$, the average energy of a beam in the specimen.

Specimen	Specimen no.	Irrad. particle and energy (MeV)	$\langle E \rangle$ (MeV)	Irrad. temp. (K)	Dose (10^{15} particles/cm^2)	Initial resistivity ρ_0(4.2 K) (Ω cm)	Resistivity increase $\Delta\rho_0$(4.2 K) (nΩ cm)
ord-Cu_3Au	1	p, 5.4	4.7	20	2.1	2.786×10^{-6}	51.3
	2	p, 5.4	4.7	15	4.0	2.746×10^{-6}	92.2
	3	p, 5.4	4.7	21	5.9	2.459×10^{-6}	133.1
	4	p, 3.6	2.7	14	1.2	2.713×10^{-6}	39.9
	5	α, 20.5	17.8	14	0.52	2.419×10^{-6}	56.5
	6	α, 20.5	17.8	30	0.86	2.480×10^{-6}	100.8
	7	α, 20.5	17.8	25	1.3	2.351×10^{-6}	160.5
dis-Cu_3Au	8	α, 20.5	17.5	13.5	1.4	9.996×10^{-6}	44.0
Cu	9	p, 5.4	5.0	20	2.1	3.88×10^{-9}	4.4
	10	p, 5.4	4.8	15	4.0	3.29×10^{-9}	11.0
	11	p, 5.4	5.0	21	5.9	4.54×10^{-9}	15.9
	12	p, 3.6	3.1	14	1.2	4.58×10^{-9}	4.5
	13	α, 20.5	17.7	14	0.52	2.85×10^{-9}	8.3
	14	α, 20.5	16.8	23	1.4	2.08×10^{-9}	14.5
	15	α, 20.5	18.3	20	1.6	3.46×10^{-9}	17.0

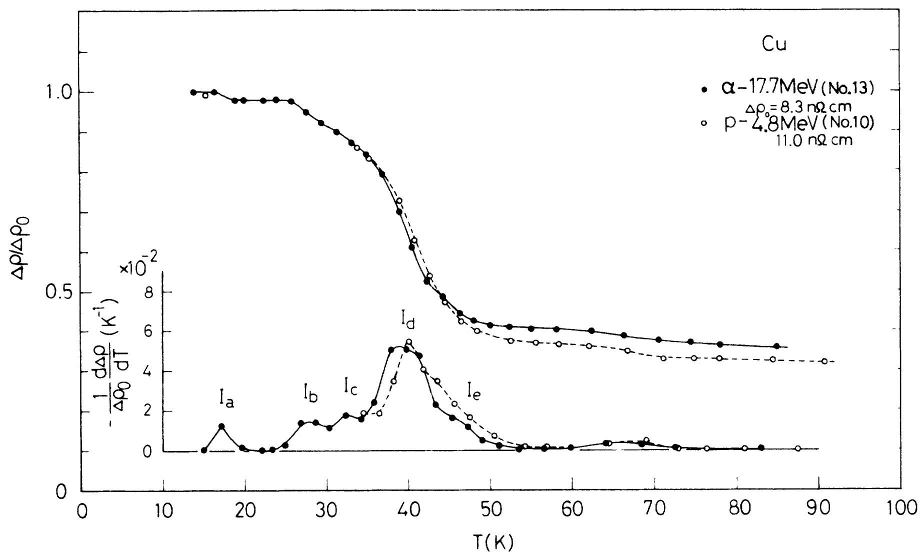

FIG. 1. Isochronal recovery curves of the electrical resistivity in 4.8-MeV-*p*-irradiated or 17.7-MeV-α-irradiated Cu. The resistivity increase $\Delta\rho_0$ is 11.0 nΩ cm for specimen 10 and 8.3 nΩ cm for specimen 13.

made to the irradiation-induced resistivity increase $\Delta\rho_0$(Cu). An experimental error is about 0.002 in a scale of $\Delta\rho/\Delta\rho_0$. Derivatives of the isochronal recovery curves are shown in the inset. As in the case of stage-I recovery in electron irradiation,[18–22] five substages Ia to Ie in order of increasing temperature were observed below 60 K, although they were not so clearly separated from each other as those in the electron irradiation. Figure 2 shows the results for other Cu specimens. As they were irradiated above 20 K, the stage Ia was not observed. From Figs. 1 and 2, it is known that the peak temperatures of stages Ib, Ic, and Id in the derivatives of the recovery curves are independent of irradiation dose, whereas that of stage Ie depends on dose and shifts to lower temperature with increasing dose. The peak temperatures of stages Ia, Ib, Ic, and Id are the same as those observed as in the electron irradiation.

Although the interpretation of stage-I recovery has been a matter of dispute,[23] the recovery of stages Ia, Ib, and Ic has been attributed to the close-pair annihilation.[20,21] The total fraction of recovery in these three substages amounts to about 15%, which is much smaller than that in electron irradiation (26–30 %) (Ref. 22) and closer to that in 10-MeV deuteron irradiation (20%).[22] The total recovery of stage I is about 64%, which is also much smaller than that in electron irradiation (86%)

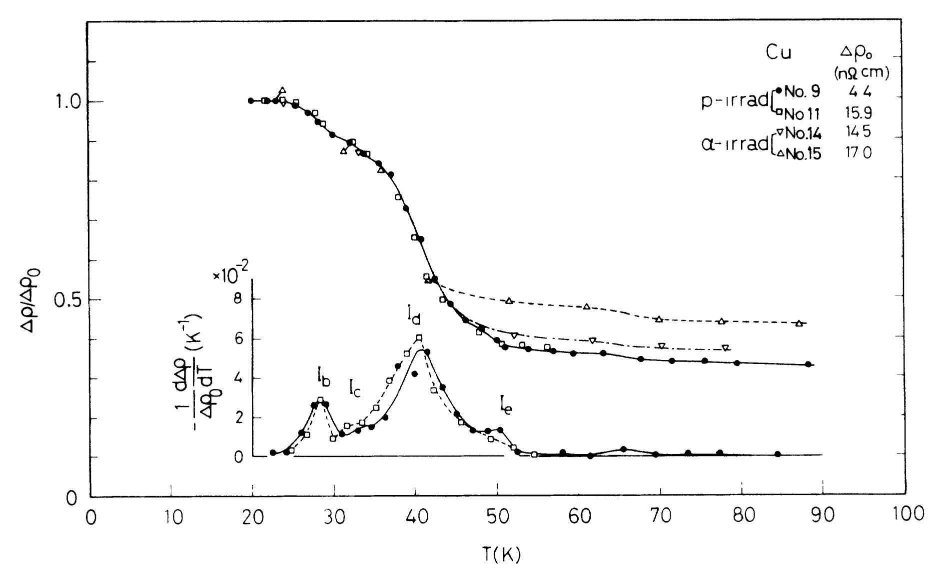

FIG. 2. Isochronal recovery curves of the electrical resistivity in (4.8–5.0)-MeV-*p*- or (16.3–18.3)-MeV-α-irradiated Cu.

(Refs. 21 and 22) and the same as that in 10-MeV deuteron irradiation.[22] As observed in Figs. 1 and 2, in the proton irradiation this fraction is slightly larger than that in the α irradiation and approximately independent of irradiation dose, whereas in the α irradiation it is dose dependent and decreases with increasing dose in the same region of irradiation-induced resistivity increase $\Delta\rho_0$(Cu) as in the proton irradiation.

Results of the irradiation with 3.1-MeV protons are shown in Fig. 3, which are similar to those of 4.8–5.0-MeV proton and 16.8–18.3-MeV α irradiations.

In all Cu specimens a small recovery stage was observed around 65 K. It would be assigned to one of the substages of stage-II recovery.[24]

B. Cu_3Au

The results of isochronal annealing of ordered Cu_3Au (ord-Cu_3Au) irradiated with 4.7-MeV protons or 17.8-MeV α particles are shown in Fig. 4. A fractional resistivity change $\Delta\rho/\Delta\rho_0$ is normalized to irradiation-induced resistivity increase $\Delta\rho_0$ (ord-Cu_3Au). An experimental error is about 0.01 in a scale of $\Delta\rho/\Delta\rho_0$. There is a difference in the annealing behavior between the proton irradiation and the α irradiation.

On the specimens irradiated with protons or with a low dose of α particles (specimens 1, 2, 3, and 5), annealing curves are divided into two parts; a small resistivity increase (reverse annealing) below 40 K and normal recovery between 40 and 90 K. Derivatives of the isochronal recovery curves above 40 K on these specimens are shown in Fig. 5. A few stages seem to exist above 40 K, but they are not clearly defined. However, it might be said that there are small substage(s) between 40 and 52 K, and a large stage around 70 K, and in between recovery proceeds continuously. The large stage shifts to lower temperature with increasing dose. The total fraction of recovery by the annealing up to 90 K is nearly the same ($\sim 20\%$) in both cases of the proton and α irradiations.

In the case of α irradiation, a large reverse annealing stage was observed above 30 K already for $\Delta\rho_0$(ord-Cu_3Au)$=101$ nΩ cm, whereas for such an amount of $\Delta\rho_0$(ord-Cu_3Au) it was not observed in the proton irradiation. Resistivity begins to increase around 33 K, reaches a maximum between 45 and 55 K, and then decreases above 55 K. It is considered that the maximum appeared as a result of competition of two processes; a reverse annealing stage and a normal recovery stage as observed in the proton and low-dose α irradiations. This normal recovery shifts to lower temperatures with increasing dose as described above.

Figure 6 shows the result on a disordered specimen, together with the results on an ordered Cu_3Au and a Cu specimen. Being different from the case of ordered specimens, in the disordered specimen recovery was almost completed at 60 K. The fraction of recovery is only about 10%. Compared with the results on Cu specimens this behavior is interpreted to mean that the stage-I recovery of Cu is strongly suppressed by doping of Au atoms.

IV. DISCUSSION

A. Damage production

For convenience for later discussion the existing experimental results on damage production are summarized here.

It has been known that in Cu_3Au long-range ordering decreases the electrical resistivity, whereas short-range ordering increases the resistivity.[25–27] The irradiation-induced resistivity increase has been considered to be due

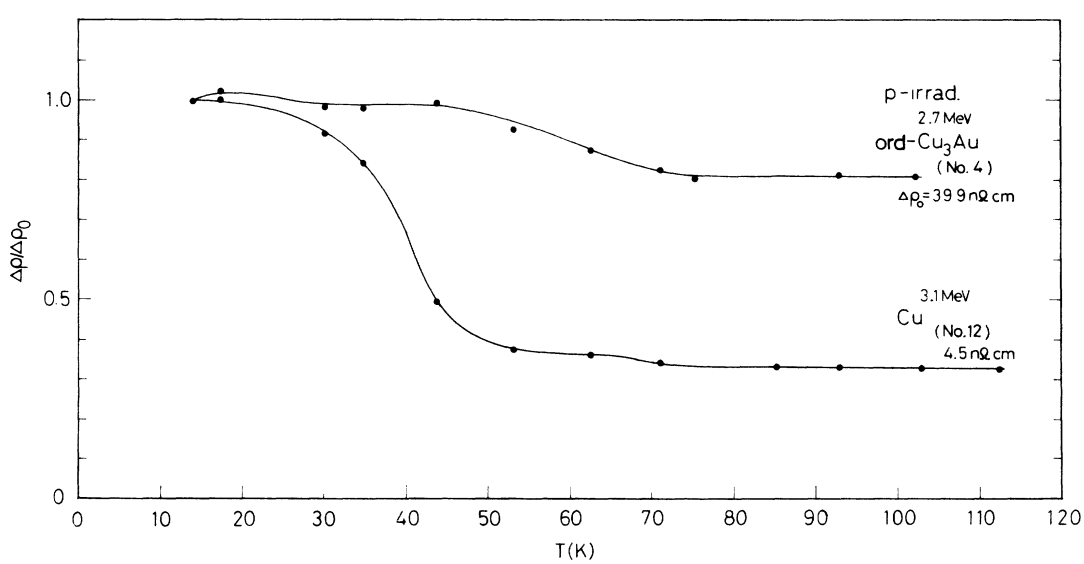

FIG. 3. Isochronal recovery curves of the electrical resistivity in proton-irradiated ordered Cu_3Au (2.7-MeV p) and Cu (3.1-MeV p). The resistivity increase $\Delta\rho_0$ is 39.9 nΩ cm for Cu_3Au and 4.5 nΩ cm for Cu.

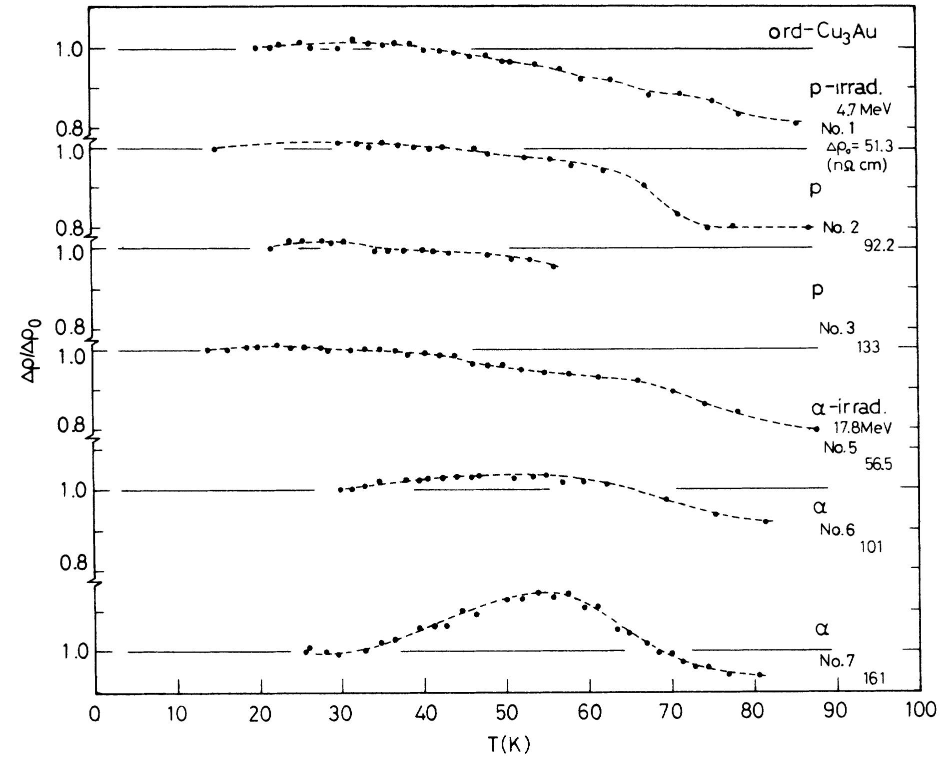

FIG. 4. Isochronal recovery curves of the electrical resistivity in 4.7-MeV-p- or 17.8-eV-α-irradiated ordered Cu_3Au. The fraction not annealed, $\Delta\rho/\Delta\rho_0$, is obtained by normalizing the resistivity increase $\Delta\rho$ to the irradiation-induced resistivity increase $\Delta\rho_0$(ord-Cu_3Au).

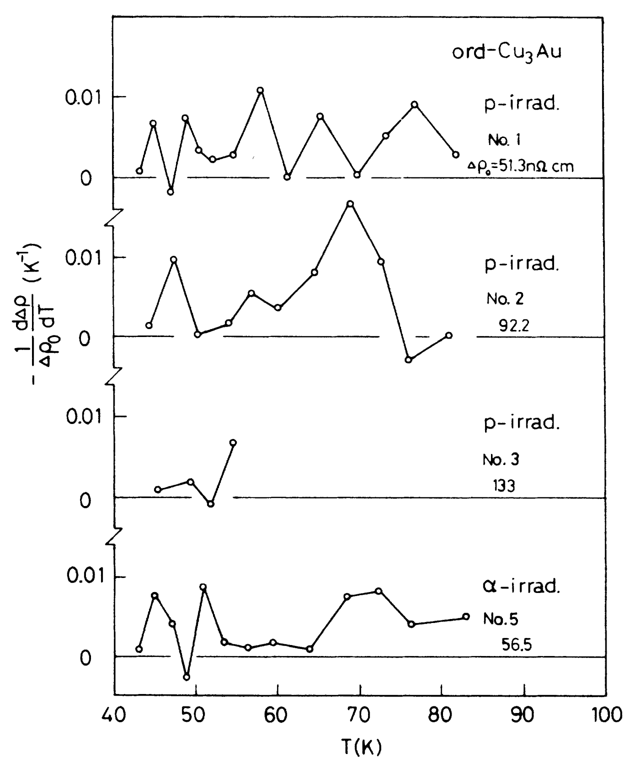

FIG. 5. Derivative isochronal recovery curves obtained from the data shown in Fig. 4.

to point defects and the decrease of long-range ordering. From the resistivity measurement under fast-neutron irradiation below 20 K the number of replacements per Frenkel pair was estimated to be about 50–70.[6,7] In proton (3.6–13.7 MeV), α-particle (20–38.5 MeV), and C-ion (72.5 MeV) irradiations below 18 K this ratio was estimated to be about 27, which was independent of irradiation energy.[10] Kirk, Blewitt, and Scott investigated damage-production mechanism at low temperature under neutron irradiation on ordered Ni_3Mn alloys having the same crystal structure as Cu_3Au.[28,29] In the case of thermal-neutron irradiation where damage is produced by (n,γ) recoil of an average energy of 450 eV, significant disordering due to $\langle 110 \rangle$ replacement collision sequences was observed. The number of replacements per recoil was 132 and these replacements were found in a quite small number of sequences, perhaps one or two sequences per recoil. This result suggests the presence of long replacement collision chains. On the other hand, in fast-neutron irradiation where typical recoil energies are 20 keV, significant random disordering was observed but no evidence for sizable replacement sequences was observed. As the average energy of primary knock-on atoms (PKA) for proton and α-particle irradiations in the present experiment is about 250 eV, damage process would be similar to that in the thermal-neutron irradiation rather than that in the fast-neutron irradiation.

The experiment by Alamo *et al.*[12] on the damage-production rate in electron irradiation with energies

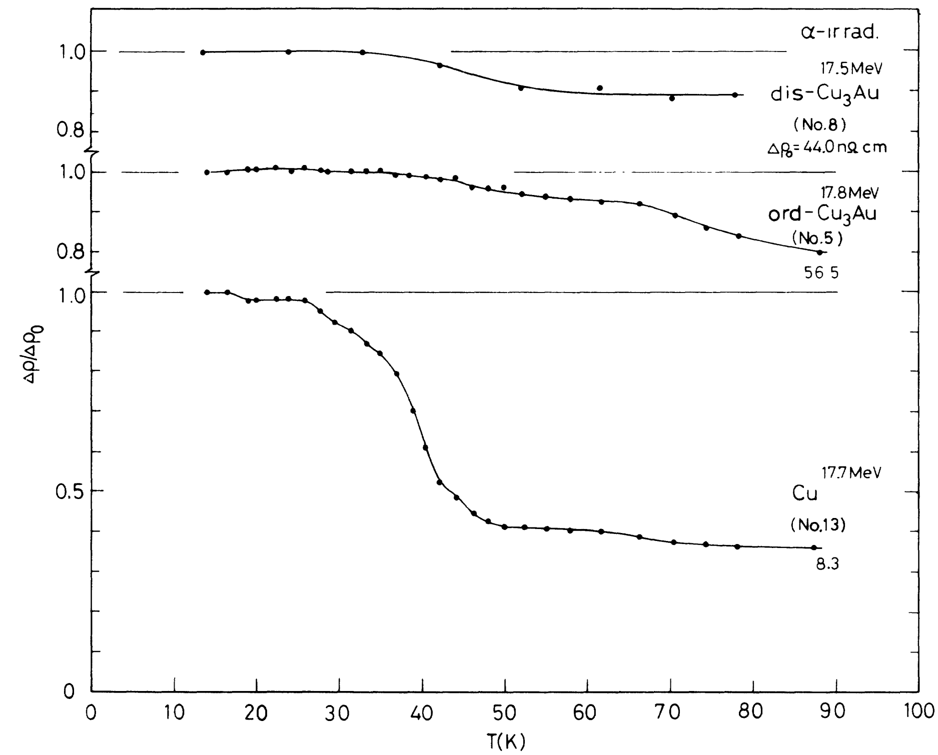

FIG. 6. Isochronal recovery curves of the electrical resistivity in α-irradiated disordered Cu_3Au (17.5-MeV α, $\Delta\rho_0=44.0$ nΩ cm), ordered Cu_3Au (17.8-MeV α, $\Delta\rho_0=56.5$ nΩ cm) and Cu (17.7-MeV α, $\Delta\rho_0=8.3$ nΩ cm).

ranging from 0.4 to 2.5 MeV indicated that the production curves can be well explained by considering that only one kind of atom is not displaced to produce stable Frenkel defects, but both kinds of atoms are displaced with similar displacement threshold energy E_d; $E_d^{\mathrm{Cu}}\simeq 24$ eV and $E_d^{\mathrm{Au}}\simeq 18$ eV. From this experiment resistivities of Frenkel pairs in ordered Cu_3Au were estimated approximately as $\rho_{\mathrm{FP}}^{\mathrm{Cu}}\simeq\rho_{\mathrm{FP}}^{\mathrm{Au}}\simeq 5$ $\mu\Omega$ cm/at. % FP.[12] In a previous paper on ion irradiation we reported the ratio of resistivity increase of disordered Cu_3Au to that of Cu to be 1.9, compared at the same damage energy density S.[10] Assuming that in ordered Cu_3Au and also disordered Cu_3Au approximately the same fraction of Cu and Au atoms are displaced and $\rho_{\mathrm{FP}}^{\mathrm{Cu}}\simeq\rho_{\mathrm{FP}}^{\mathrm{Au}}$, and that these resistivity values are the same in both states, the specific resistivity of Frenkel pairs in ordered Cu_3Au can be estimated from the ratio described above as $\rho_{\mathrm{FP}}^{\mathrm{Cu}}\simeq\rho_{\mathrm{FP}}^{\mathrm{Au}}\simeq 4.8$ $\mu\Omega$ cm/at. % FP by taking $\rho_{\mathrm{FP}}^{\mathrm{Cu}}\simeq 2.5$ $\mu\Omega$ cm/at. % FP in pure Cu. This is very similar to the value estimated by Alamo *et al.*[12]

In a previous paper on ion irradiation it was also reported that the ratio of resistivity increase of ordered Cu_3Au to that of Cu was 7.3 for the same value of S, being independent of S, i.e., independent of the irradiation energy.[10] These results indicate that the ratio of damage rates between ordered and disordered Cu_3Au is 3.84, independent of the irradiation energy. Therefore, it is considered that the fraction of $\frac{1}{3.84}$ of irradiation-induced resistivity in ordered Cu_3Au, $\Delta\rho_0$(ord-Cu_3Au), is associated with that due to Frenkel pairs $\Delta\rho_{0,\mathrm{FP}}$(ord-$Cu_3Au$) [$=\Delta\rho_0$(ord-$Cu_3Au$)/3.84].

B. Recovery between 40 and 90 K in ordered Cu_3Au

The recovery stages observed between 40 and 90 K in ordered Cu_3Au are assigned to those associated with Cu interstitials as described in the following.

According to Brinkman, Dixon, and Meechan[5] and also the result of neutron-irradiation experiments,[6] the migration of interstitials does not produce ordering in Cu_3Au. A large resistivity recovery has been observed around 280 K (Ref. 7) or 320 K (Ref. 6) in neutron irradiation, around 240 K (Ref. 11) or 300 K (Refs. 13 and 30) in electron irradiation, and around 290 and 400 K in ion irradiation.[8] In many cases the resistivity decreased to a lower value than the preirradiation value. This result suggests the occurrence of the recovery of ordering. Positron annihilation experiments on 3-MeV-electron-irradiated ordered Cu_3Au indicated that single vacancies migrate at 260 K.[31] The recovery stage above 240 K is attributed to the long-range migration of vacancies. Hence the recovery stages below 90 K are considered to be related to the interstitial migration.

In ordered Cu_3Au, all 12 nearest-neighbor sites of a Au atom are occupied by Cu atoms. Although there is no information on the configuration of Au interstitials, Au interstitials may be unstable and it seems to be very difficult for them to make long-range migration retaining their configuration. On the other hand, each Cu atom is surrounded by eight Cu atoms and four Au atoms, and half of the {100} planes are occupied by only Cu atoms. It is possible for Cu interstitials to make long-range migration in a Cu sublattice, although the movement is dimensionally restricted. According to recent Huang diffuse scattering experiments on electron-irradiated ordered Cu_3Au at low temperatures,[30] the relaxation volume of interstitials is small ($\sim$0.8 atomic volume), which is attributed to smaller Cu atoms, and at the end of a large recovery stage around 100 K small interstitial clusters, especially di-interstitials, are formed. Therefore, the large recovery stage around 70 K observed in the present experiments, which is dose dependent, is assigned to that associated with long-range migration of Cu interstitials. The small recovery stages between 40 and 52 K are considered to be stages for close-pair recovery of Cu Frenkel pairs. Such a lower-temperature small stage has also been observed around 35 K in electron irradiation[13] and around 40 K in neutron irradiation.[7] In the low-temperature close-pair recovery, close pairs having various separation distances might be engaged. Correspondingly, their recovery temperatures are different.

The total fraction of recovery of Frenkel pairs between 40 and 90 K in ordered Cu_3Au is nearly the same as that of state I in Cu. This fraction was estimated by renormalizing the recovered resistivity to $\Delta\rho_{0,FP}$(ord-Cu_3Au) instead of $\Delta\rho_0$(ord-Cu_3Au). The result is shown in Fig. 7. The renormalized fractions of recovery on various specimens are listed in Table II. The total fraction of recovery up to 85 K in ordered Cu_3Au was about 70% and that of stage I in Cu was 64%.

As to the recovery of disordered Cu_3Au, different from the recovery of Cu and ordered Cu_3Au, long-range migration of interstitials below 90 K was suppressed. Gilbert *et al.* made isochronal annealing experiments on disordered specimens irradiated with 1.0-MeV and 1.5-MeV electrons with doses of around 10^{18} cm^{-2}.[11] In the 1.5-MeV irradiation new recovery stages were observed at 55 and 190 K in addition to stages at 90 and 130 K observed in the 1.0-MeV irradiation. The stages at 55 and 90 K were assigned to close-pair recovery of Au Frenkel pairs and Cu Frenkel pairs, respectively. Being different from the above results, in other experiments on 2.4-MeV electron irradiation with a dose of 2×10^{19} cm^{-2} (Ref. 13) and neutron irradiation,[6,7] distinct stages were not observed but recovery proceeded continuously up to 250 K. The central temperature of the recovery stage observed in the present experiment is about 45 K. This stage corresponds probably to that observed at 55 K in the electron irradiation.

C. Reverse annealing below 40 K

The small resistivity increase below 40 K, which was observed in both proton and α irradiations, would be associated with Au interstitials. According to the result of electron-irradiation experiments, approximately the same fraction of Au atoms as that of Cu atoms are displaced and $\rho_{FP}^{Cu} \simeq \rho_{FP}^{Au} \simeq 5$ $\mu\Omega$ cm/at. % FP in ordered Cu_3Au.[12] One of the possible explanations for this small resistivity increase is that it is due to the conversion of a Au interstitial to an antistructure defect (a Au atom at a Cu site) and a Cu interstitial. If it is assumed that the resistivities associated with a Au interstitial and a Cu interstitial are the same from the analogy to the relation on the resistivities of Frenkel pairs, this conversion increases the resistivity by 0.4 $\mu\Omega$ cm per percent of converted Au interstitials, because for a completely ordered specimen the resistivity increase per percent of replacement has been es-

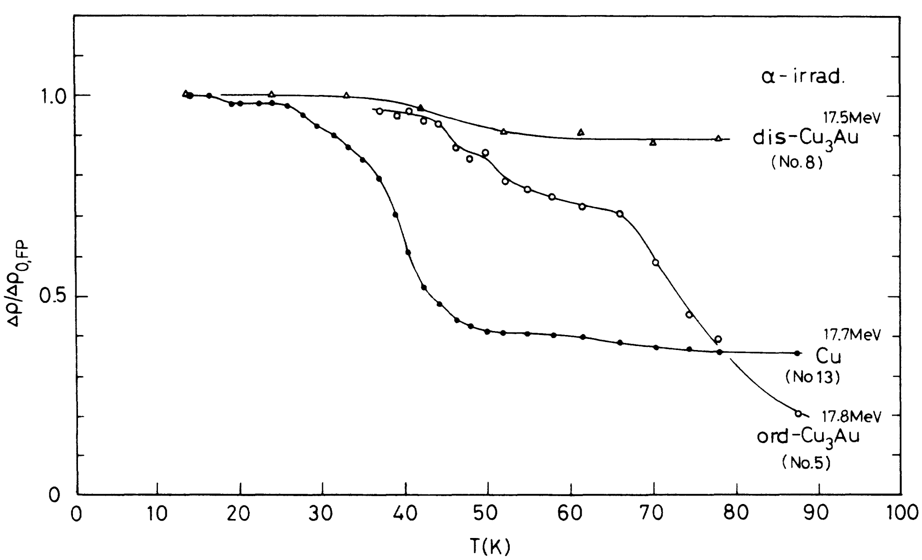

FIG. 7. Isochronal recovery curves of the electrical resistivity in α-irradiated disordered Cu_3Au, ordered Cu_3Au, and Cu. The curves for disordered Cu_3Au and Cu are the same as those in Fig. 6. The curves for ordered Cu_3Au were obtained from the curve in Fig. 6 by renormalizing the resistivity increase $\Delta\rho$ to the resistivity increase due to Frenkel pairs $\Delta\rho_{0,FP}$(ord-Cu_3Au).

TABLE II. The fraction of recovery in stage I relative to the resistivity increase due to Frenkel pair formation $\Delta\rho_{0,\mathrm{FP}}$. The figures in parentheses for ordered Cu_3Au represent the fraction of recovery relative to the irradiation-induced resistivity increase $\Delta\rho_0$.

Irrad.	Specimen	Specimen no.	Resistivity increase $\Delta\rho_0$(4.2 K) (nΩ cm)	Fraction of recovery up to 60 K (%)	Fraction of recovery up to 85 K (%)
4.7-MeV p	ord-Cu_3Au	1	51.3	~31 (~8)	~71 (18.5)
		2	92.2	~19 (~5.2)	~76 (~19.9)
		3	133.1		
2.7-MeV p	ord-Cu_3Au	4	39.9		~74 (19.3)
17.8-MeV α	ord-Cu_3Au	5	56.5	~27 (~7)	~73 (19.0)
17.5-MeV α	dis-Cu_3Au	8	44.0	~11	~11
5.0-MeV p	Cu	9	4.4	~64	
3.1-MeV p	Cu	12	4.5	~64	
17.7-MeV α	Cu	13	8.3	~60	

timated to be 0.4 $\mu\Omega$ cm.[6]. Therefore, if all Au interstitials would be converted below 40 K, the increase of about 2% of total irradiation-induced resistivity due to Frenkel pairs, $\Delta\rho_{0,\mathrm{FP}}$(ord-$Cu_3Au$), $(\frac{1}{4}\frac{0.4}{5})$, would be expected. The observed resistivity increase is about 1% of the total irradiation-induced resistivity $\Delta\rho_0$(ord-Cu_3Au), and it amounts to about 3.8% of $\Delta\rho_{0,\mathrm{FP}}$(ord-$Cu_3Au$). This is the same order of magnitude as the expected value. Such a resistivity increase due to antistructure defects is not expected in a disordered state, which is consistent with the experimental results.

Below 40 K this reverse annealing appears as a small peak. This would be a result of two competing processes; a process of resistivity increase described above and a process of resistivity recovery. One of the possibilities for the latter process would be close-pair Au-interstitial–vacancy recombination: An isolated Au interstitial is converted to a Cu interstitial and an antistructure defect, while Au interstitials close to vacancies recombine with vacancies. In the latter process the recombination of Cu-interstitial–vacancy close pairs, which are separated at much smaller distances than those considered for the stages above 40 K, might be also engaged.

D. Large reverse annealing above 30 K

This annealing behavior cannot be clearly explained at the present stage, but the following discussions will be made. This reverse annealing as observed only in the α irradiation. It becomes more conspicuous with increasing dose. These results suggest that this annealing stage is closely related to a difference in the spatial distribution of defects between proton and α irradiations. The presence of such a difference is supported by the results on Cu (Figs. 1 and 2) that in the α irradiation the total fraction of stage-I recovery decreased with increasing dose and it was not the case in the proton irradiation. As the resistivity increase in the reverse annealing occurs over the wide temperature range from 33 to 55 K, various processes having different activation energies may be engaged in. This temperature range is lower than that for long-range migration of Cu interstitials. Therefore, it is considered that this resistivity increase does not result from the long-range migration of interstitials, but from a process of a small number of jumps, i.e., an interaction between closely located defects, for example, interstitial clustering. In addition, this reverse annealing was not observed in disordered Cu_3Au and in Cu for the same irradiation dose as in ordered Cu_3Au. Therefore, this resistivity increase is peculiar to the ordered state; probably a similar process takes place in these three kinds of specimens, but only in the ordered state is it observed as a resistivity increase.

In ion irradiation in the MeV region a number of cascades are created by PKA; defects are distributed inhomogeneously. With increasing dose the cascades overlap to each other and the overlapped region contains a higher density of defects. The reverse annealing might be related to the presence of such regions.

In ordered Cu_3Au the cascades are observed as disordered zones by the electron microscopy.[15] Cu^+-ion-irradiation experiments demonstrated that the cascade size becomes larger with increasing PKA energy E_p, and at $E_p > 30$ keV a cascade consists of a bundle of several subcascades.[16] According to the electron microscopic observation on ordered Cu_3Au irradiated with 3.5-MeV p or neutrons at room temperature, in the 3.5-MeV p irradiation a damage structure consists of isolated single cascades with mean diameter of about 55 Å, most of which are produced by PKA's of energies of 10–30 keV.[16] On the other hand, in 14-MeV fusion neutron irradiation the cascades are larger (a mean diameter ~144 Å) and each cascade consists of several subcascades of 70–80 Å, reflecting that in the fusion neutron irradiation the fraction of high-energy PKA's is larger than in the 3.5-MeV p irradiation.[16] Therefore a size distribution of cascades depends on the PKA energy spectrum.

It is estimated that as in the 3.5-MeV p irradiation, in the 4.7-MeV p and 17.8-MeV α irradiations in the present study most of the defects (>75%) are produced by

PKA's below 30 keV. The average energy of E_p is not significantly different in both irradiations because of the $1/E_p^2$ dependence of a cross section for production of PKA's of E_p; about 250 eV for the 4.7-MeV p and 290 eV for the 17.8-MeV α irradiation. However, the maximum energy of E_p of Cu recoils is much different: 0.29 and 3.8 MeV for Cu recoils in the 4.7-MeV p and 17.8-MeV α irradiations, respectively. Therefore the difference between two irradiations is that the fraction of higher-energy PKA's in the 17.8-MeV α irradiation is larger than in the 4.7-MeV p irradiation. As described above, a high-energy cascade consists of closely distributed subcascades and, therefore, defects are highly concentrated within small regions. If the cascades overlap to each other, small regions containing a much higher density of defects are produced.

When defects are distributed locally in high density, there are possibilities for recombination of close pairs of a Cu interstitial and a Au vacancy or a Au interstitial and a Cu vacancy, and for the clustering of interstitials to take place by a small number of jumps if their interaction is strong, in addition to close-pair recovery of Cu or Au Frenkel pairs. The first two recombination processes do not increase the resistivity, because the resistivity decrease due to the annihilation of an interstitial and a vacancy overcomes the increase due to the formation of an antistructure defect. If the clustering of interstitials would increase the resistivity as the short-range ordering does, the reverse annealing is expected.

If the clustering of interstitials is responsible for the reverse annealing, the observed dose dependence is considered to be the result of the overlapping of cascades, which takes place with increasing dose. As described above, in both irradiations in question, most of cascades are produced by PKA's of 10–30 keV. The mean separation between collision events to produce PKA's of 10–30 keV was estimated from a Rutherford scattering cross section to be about 550 and 570 Å for specimens 3 (4.7-MeV p irradiation) and 7 (17.8-MeV α irradiation) having approximately the same $\Delta\rho_0$(ord-Cu_3Au) value, respectively. This difference is small. As the mean size of cascades produced by PKA's of 10–30 keV is about 55 Å,[16] the probability for overlapping of such cascades would be nearly the same and small in both specimens. Even if the overlapping would take place, it would not induce the difference in annealing behavior in both specimens. Therefore, the overlapping of such small cascades and large ones produced by PKA's of high-energy E_p would play an important role, because the fraction of high-energy cascades is larger in the 17.8-MeV α irradiation than in the 4.7-MeV p irradiation. When the large cascades are produced around antiphase boundaries (APB's) the interstitial clustering would be enhanced. Electron microscopic observation on the electron irradiation of ordered Cu_3Au at 300 K demonstrated that there is a strong preference for the precipitation of interstitial clusters on the APB's.[14] This result suggests that the APB acts as a nucleation center for the interstitial clustering.

In fission neutron irradiation by Alamo *et al.* the reverse annealing was not observed even for large $\Delta\rho_0 = 1.2$ $\mu\Omega$ cm.[7] The difference with the present result is probably due to the difference in the state of specimens such as the density of APB, the nonstoichiometry, and the state of order, and/or due to that the PKA energy spectrum and the cascade size distribution in the fission neutron irradiation are similar to those in 3.5-MeV proton irradiation rather than to 14-MeV fusion neutron irradiation,[16] although it depends on the energy spectrum of fission neutrons in question, and hence the fraction of high-energy cascades is small. The comparison of cascade structures in Au between fission neutron and fusion neutron irradiations by electron microscopy revealed that the average number of subcascades in a cascade is 2.2 in the fission neutron irradiation and 6.7 in the fusion neutron irradiation, and that the cascade size in the fission neutron irradiation is much smaller than that in the fusion neutron irradiation.[32]

Besides the difference in cascade distribution, the following effect is also to be noted. Recent 14-MeV-neutron-irradiation experiments on Au indicated that vacancy-type clusters are formed at temperatures at which isolated vacancies are immobile.[17] This dynamical effect is characteristic of high-energy irradiation. When such clusters are formed, sink density changes and annealing behavior is affected. As this type of dynamical effect is considered to be different between the 4.7-MeV p and 17.8-MeV α irradiations, this effect also has to be taken into account in the interpretation of annealing behavior.

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