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Annealing experiments on dilute *Pb*Au alloys after electron irradiation at 6 K

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The resistivity annealing spectra of electron-irradiated dilute *Pb*Au alloys (24 – 650 at. ppm Au) have been measured over the temperature range 6 – 320 K. The experiments were performed to examine the possibility of forming Au-Pb diplons from lead interstitials, created during the electron irradiation at 6 K, migrating to and being trapped by gold atoms in substitutional sites. The alloys were quenched prior to irradiation in order to obtain a measurable proportion of gold atoms on substitutional sites. Although the annealing spectra showed stages which were dependent on the Au impurity, it was not possible to relate any of the stages uniquely to the formation of a Au-Pb diplon.

I. INTRODUCTION

Fast impurity diffusion has been observed in a considerable number of metals and the subject has been reviewed in detail.[1] In general, the impurity is a noble or late transition metal and the solvents are lead, tin, thallium, indium, the alkali metals, zirconium, titanium, and some of the rare earths. The experimental evidence supports the hypothesis that the impurities are diffusing primarily by an interstitial mechanism.[1] Not all of the impurity atoms are in interstitial sites and to explain the diffusion of copper in germanium, Frank and Turnbull[2] proposed a dissociative model. In this model the solute dissolves in both interstitial and substitutional sites and the effective diffusion coefficient can be written as $D_{\text{eff}} = D_i X_i + D_s X_s$, where the X's are the equilibrium fractions of interstitials and substitutionals, and D_i and D_s are their respective diffusion coefficients. This model has been extended by both Miller[3] and Decker *et al.*[4] to include other types of defect complexes, and has been widely applied in interpreting the data for these fast impurity diffusion systems. There is discussion on whether the experimental evidence requires more than a simple model involving single defects and substitutional dimers,[5–11] but the case for considering higher-order clusters does not appear strong.[8–10] The literature has been recently reviewed[1,5] and will not be cited here.

The most studied system is probably *Pb*Au. However, even for this system the exact nature of the different defects and their distribution as a function of temperature is still not clearly understood.[6–12] The evidence (linear Arrhenius plot of the diffusivity) suggests that from the melting temperature to at least 333 K the diffusion of gold in lead is dominated by interstitial diffusion, $D_{\text{eff}} = X_i D_i$.

The atomic configuration of the interstitial is not known, but it has been suggested[1,6,7,13–15] that the defect might be a split or dumbbell-type interstitial, referred to as a diplon,[1] i.e., two atoms, a Au-Pb pair sharing a lattice site, but each displaced from it in opposite directions along a ⟨100⟩ direction. LeClaire[5] has discussed the diplon model and pointed out that such a model provides a satisfactory explanation for the low mass effects for diffusion of noble metals in lead.[16–18] From irradiation damage experiments in dilute alloys it is well known[19] that most impurities in metals are traps for migrating self-interstitials produced by the irradiation. Simple model calculations by Dederichs[20] predict that mixed dumbbells (dumbbells in which one of the regular dumbbell atoms is replaced by the impurity atom) are formed when undersized impurities trap self-interstitials in accordance with experimental observation.[21,22] Model calculations[20] of the elementary jumps of the impurity-interstitial complex predict a cage motion of the impurity atom, which has been observed at quite low temperatures,[22,23] as well as a reorientation of the mixed dumbbell on its site by 90°. The combination of these two processes leads to long-range migration of the complex as a unit. Radiation-enhanced solute segregation studies have shown that solute transport could be explained by the migration of mixed dumbbells.[24] As pointed out by Schilling[25] this diffusion process is identical with that of the diplon mechanism. Recent lattice parameter measurements[8] have shown that Au dissolution in Pb produces a lattice contraction and thus raises the possibility of the formation of Au-Pb diplons due to trapping of migrating Pb self-interstitials by Au atoms dissolved in Pb.

There is one piece of previous evidence which suggests diplons may indeed be found during irradiation. The tracer diffusion studies of Au in Pb have always shown strong evidence for dehancement unless the Au concentration is kept very low.[9] However, even for low Au concentrations, at low diffusion annealing temperatures[9,26,27] the concentration profiles found from thin-film radiotracer sectioning experiments showed a strong tendency toward non-Gaussian behavior. This has been interpreted by Decker *et al.*[9] to result from the trapping of tracer in immobile substitutional dimer states near the sample surface where the gold concentration is larger. Barbu[27] made diffusion anneals of Au in Pb over a range of temperatures and found that at the low temperatures where non-Gaussian behavior was observed the Gaussian profile was attained if the anneal was made under thermal neutron irradiation. The neutrons could have been breaking up the substitutional dimers, or the interstitial lead atoms generated by the irradiations could have been reforming the Au-Au diplons into Au-Pb diplons.

The present experiments proposed (1) to test the assumption that Au atoms on substitutional sites in Pb trap migrating lead self-interstitials to form Au-Pb diplons and (2) to determine the activation energy for migration of the diplon. The concept was: (1) to quench dilute alloys of *Pb*Au (24–650 at. ppm Au) in order to obtain a measurable proportion of the gold atoms on substitutional sites and (2) to irradiate the alloys with electrons at temperatures where the interstitial atoms generated by the irradiation would be mobile and might be expected to be trapped at gold atoms to form Au-Pb diplons. Subsequent annealing studies would investigate whether such diplons were indeed formed and provide a method of studying the annealing kinetics and determining the activation energy for migration. The *Pb*Au system was chosen because of the large number of previous studies; the detailed electron irradiation studies of pure lead[28] provided a base line for the annealing spectra with which to compare the *Pb*Au data. The availability of high-specific-activity gold isotopes allowed the alloy samples to be made with well-determined gold concentrations.[11]

II. SAMPLE PREPARATION

Lead, of purity 99.999%, was obtained from Metallurgie Hoboken Overpelt. The residual resistivity of the lead samples, extrapolated to zero magnetic field, gave resistivity ratios of 4500. Standardized radioactive ^{195}AuCl$_3$ was diluted with known concentrations of AuCl$_3$ and the gold was electroplated onto both ends of lead rods (1 cm diameter, 1 cm long). The electroplated Au was diffused into the lead at 220 °C. By this procedure Pb with (300 ± 15) at. ppm Au and Pb with (650 ± 30) at. ppm Au were prepared. The concentration of Au was measured by counting the radioactive ^{195}Au. The homogeneity of the solution was measured to be $\pm 5\%$. More dilute *Pb*Au alloys were prepared by melting weighed portions of these master alloys with pure lead in graphite crucibles in an induction furnace under a pressure of less than 10^{-8} bar. The concentrations of the alloys were 24, 64, 120, 302, and 650 at. ppm Au. The material was rolled between stainless-steel foils to a thickness of about 50 μm. After each rolling step, the surfaces of the dilute *Pb*Au foils and those of the stainless-steel foils were cleaned with acetone. Resistance samples (2 cm long and 0.1 cm wide) were cut from the foils. After all of the measurements of the resistivity were completed, the concentration of Au in each specimen was remeasured by counting the radioactive ^{195}Au. The decay of ^{195}Au during the time occupied by the sample preparation and the measurements of the resistivity was accounted for by comparing the radioactivity of the samples with that of the starting solution as a standard.

III. EXPERIMENTAL PROCEDURE

Ten specimens were mounted onto a sample holder which fitted into a helium cryostat (details are given in Ref. 28). Up to three specimens were irradiated simultaneously at 4.7 K with 3-MeV electrons at current densities of 10 μA cm^{-2}. After each of the ten samples was irradiated to the desired dose, they were isochronally annealed for

10 min periods at temperature intervals of $\Delta T/T = 0.05$ and the recovery of the radiation-induced residual resistivity increase $\Delta\rho$ was measured. The samples were heated by pulling the sample holder into He-gas-filled ovens preheated to the desired temperature and controlled to better than 0.1%. The residual electrical resistivity was measured at 4.2 K in a longitudinal magnetic field of 2.2 kG, which transforms Pb and the dilute *Pb*Au alloys from the superconducting into the normal conducting state.

Two irradiations were performed on the *Pb*Au alloys for two different initial states of solution of the Au atoms. We will define:

(a) *Q*-state alloys, which were obtained by quenching the mounted speciments from 493 to 4.2 K at an initial quenching speed of 200 $\mathrm{K\,s^{-1}}$. The resistivity contribution per unit concentration of Au, $\Delta\rho_{\mathrm{Au}}$, was independent of the Au concentration with $\Delta\rho_{\mathrm{Au}} = (4.05 \pm 0.22)\times 10^{-10}\Omega$ cm/at. ppm Au.

(b) $Q+A$-state alloys, which were prepared by annealing *Q*-state alloys for 10 min at 60 °C. This heat treatment leads to a 10% decrease of $\Delta\rho_{\mathrm{Au}}$ caused by partial precipitation of Au into the form of the intermetallic compound $\mathrm{AuPb_3}$.

IV. DATA AND RESULTS

Figure 1 shows the recovery of $\Delta\rho$, normalized to the maximum radiation-induced resistivity increment $\Delta\rho_0$, as a function of annealing temperature for pure Pb and different dilute *Pb*Au alloys in the *Q* state. The Au concentration C_{Au}, and $\Delta\rho_0$ are given as parameters. A value of $\Delta\rho_0 = 1$ nΩ cm corresponds approximately to 1 at. ppm of Frenkel defects.[29] The recovery of $\Delta\rho_0$ for pure Pb and the *Pb*Au alloys in the $Q+A$ state is given in

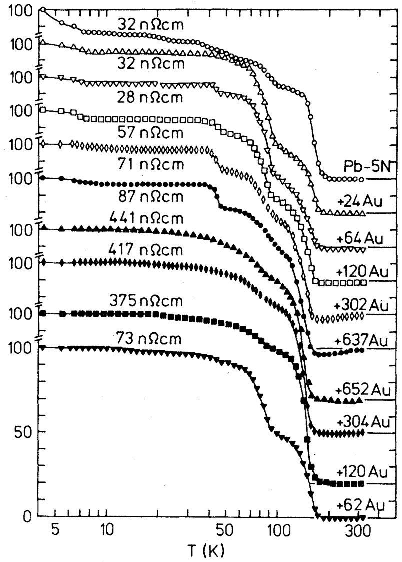

FIG. 2. Recovery of radiation-induced residual resistivity of quenched and annealed samples. Pb-5*N* means 99.999% pure Pb. The numbers preceding Au represent ppm.

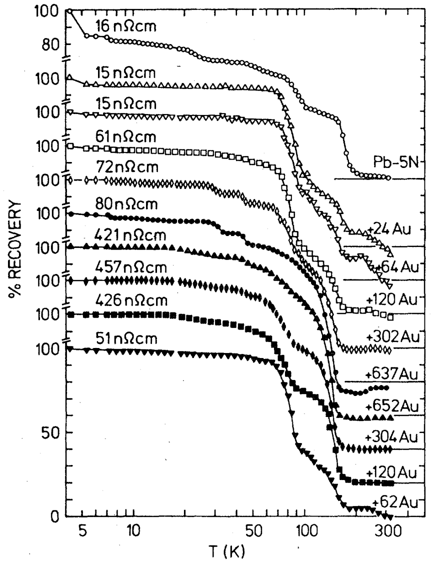

FIG. 1. Recovery of radiation-induced residual resistivity of quenched samples. Pb-5*N* means 99.999% pure Pb. The numbers preceding Au represent ppm.

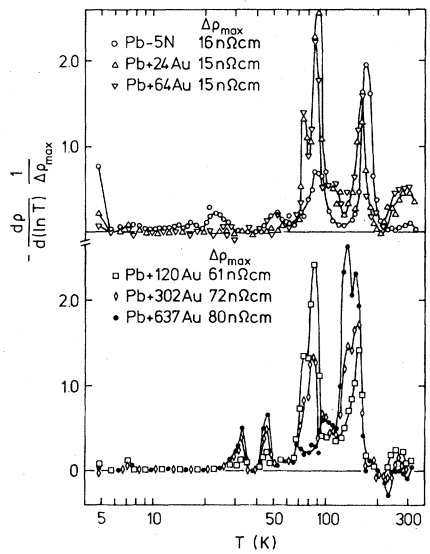

FIG. 3. Differential recovery curves for *Pb*Au alloys from the quenched state. Pb-5*N* means 99.999% pure Pb. The numbers preceding Au represent ppm.

Fig. 2. In Figs. 3–6 the dependence of the differential isochronal recovery on Au concentration, Frenkel defect concentrations, and the state of the alloys is compared. A number of peaks are observed both in pure Pb as in dilute *Pb*Au. Earlier studies[28] of pure Pb observed eight peaks in stages II (i.e., 10– 120 K). A comparison of the present data for pure Pb with those published preivously[28] shows that while some peaks occur at the same temperature, other peaks do not.

In the case of the dilute *Pb*Au alloys, up to seven annealing peaks are observed, four of which occur in stage II. (The present nomenclature for the subpeaks does not follow the pattern started for pure Pb.[28]) Stage II a occurs at 32.6 K and stage II b at 46 K, independent of the initial defect concentration. Stage II a occurs only in the Q-state alloys at low dose irradiations and increases with increasing C_{Au}. Alloys in the $Q+A$ state exhibit a larger stage II b than those in the Q state. In both alloy states stage II b increases with increasing C_{Au} and decreases with electron dose. Stage II c forms a double peak, II c′ and II c″, which cannot be well separated in all cases. Figure 7 shows the dependence of the temperature of the peaks II c′ and II c″ on the recovery occuring within this double peak. The position of II c′ seems to be independent of the defect concentration, whereas II c″ shifts to lower temperatures with increasing dose. The fractional recovery of II c′ and II c″ decreases with increasing C_{Au}, increasing dose, and is smaller in the $Q+A$ state than in the Q-state alloys. The ratio of the peak heights II c″/II c′ is independent of dose and state of the alloy, and decreases only little with increasing C_{Au}.

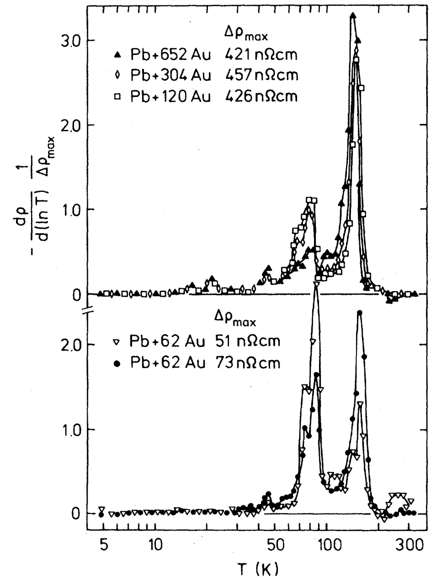

FIG. 4. Differential recovery curves for *Pb*Au alloys from the quenched state (▲, ◊, □ , ▽) and the quenched and annealed state (●). The numbers preceding Au represent ppm.

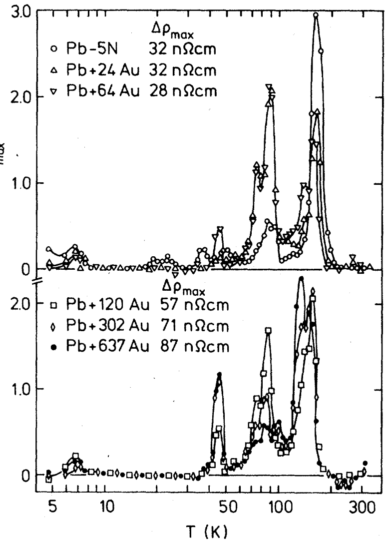

FIG. 5. Differential recovery curves for *Pb*Au alloys from the quenched and annealed state. Pb-5N means 99.999% pure Pb. The numbers preceding Au represent ppm.

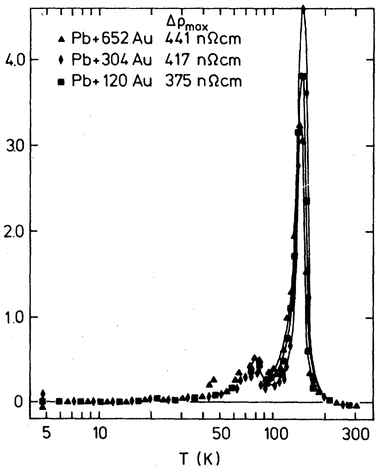

FIG. 6. Differential recovery curves for *Pb*Au alloys from the quenched and annealed state. The numbers preceding Au represent ppm.

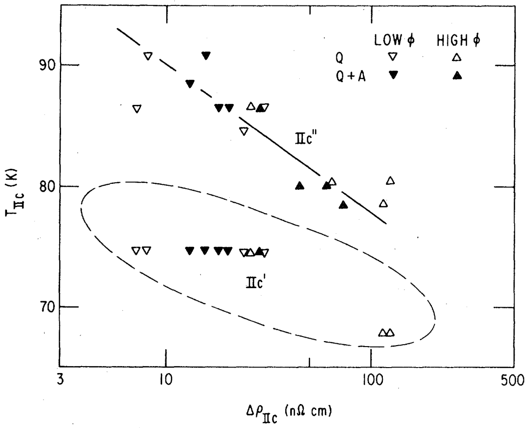

FIG. 7. Dependence of the annealing temperature of the stage II c′, and II c″ peaks on the recovery occurring within the peak. The numbers preceding Au represent ppm.

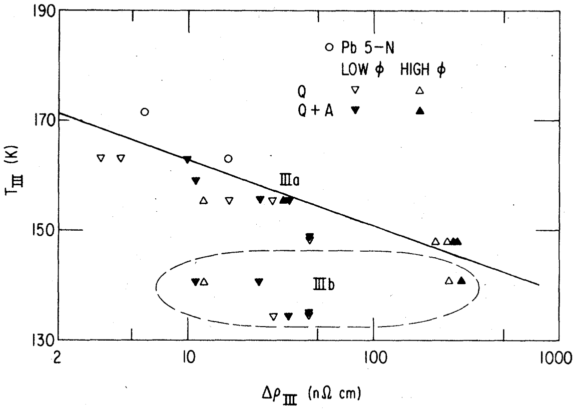

FIG. 8. Dependence of the annealing temperatures of the stages III a and III b peaks on the recovery occurring within the peak. The straight line is a fit to the data of Schroeder and Schilling (Ref. 28). Pb-5*N* means 99.999% pure Pb. The numbers preceding Au represent ppm.

Stage III consists also of the double peak labeled III a and III b. Figure 8 shows the dependences of the temperatures at which stages III a and III b occur on the recovery in that stage. The straight-line fit to the data for pure Pb measured by Schroeder and Schilling (Ref. 28, Table I) is also shown. Within experimental accuracy, the dose dependence of stage III is the same as in pure Pb, independent of C_{Au}. This result would be modified to some extent if the double peak were deconvoluted and only the recovery occurring in stage II b was plotted. An estimate showed that the data would follow a straight line parallel to the one shown in Fig. 8, but shifted by about 4 K to lower temperatures. Stage III a, which does not shift with dose, occurs only after low-dose irradiations in both the Q and the $Q+A$ state, and increases in magnitude with increasing C_{Au}. Another state labeled IV occurs at about 250 K in the Q-state alloys, and decreases in magnitude with increasing C_{Au}. The properties of the annealing stages in the irradiated *Pb*Au alloys have been summarized in Table I.

V. DISCUSSION

During the irradiation at 6 K, lead self-interstitials are mobile and will survive recombina-

TABLE I. Dependence of annealing stages of alloy, electron dose, and Au concentration (see text). The symbol X indicates the existence of the annealing stage and symbol 0 its absence. The relative magnitudes of the peaks are indicated by >, <, or = signs. The arrows in column seven are used to indicate an increasing peak magnitude, with increasing gold concentration (→) or with decreasing gold concentration (←), or 0 if independent of gold concentration.

		Dependence of peak height on:							
		State of alloy			Electron dose			Gold concentration	
Stage	Temperature of peak	Q		$Q+A$	Low ϕ		High ϕ	Low	High
II a	32.6	X		0	X		0	→	
II b	46	X	<	X	X	>	X	→	
II c ′	75	X	>	X	X	>	X	←	
II c ″	75−90	X	>	X	X	>	X	←	
III a	135−140	X	=	X	X	>>	X	→	
III b	140−170	X		X	X		X	0	

tion with vacancies only in the form of agglomerates nucleated at impurities acting as trapping centers. During the subsequent isochronal anneal, the radiation-induced resistivity $\Delta\rho$ will recover when : (a) interstitial-impurity complexes dissociate and the detrapped interstitials recombine with vacancies, (b) interstitial-impurity complexes migrate and react with vacancies, (c) rearrangement of these complexes causes a change of the resistivity, (d) when vacancies become mobile in stage III.

The presence of a number of annealing stages characteristic of the dilute *Pb*Au alloys indicates that a number of different interstitial-impurity complexes were formed during the irradiation. Although we cannot exclude the possibility that single substitutional Au atoms alone can lead to a number of different interstitial-impurity complexes, the dependence of the peak heights on the state of the alloy, electron dose, and C_{Au} suggests that Au atoms are present in at least two different configurations. We have estimated that the quench rate (200 K s^{1}) was fast enough to retain measurable proportions of gold on substitutional sites, but too slow to retain any Au atoms in the interstitial state. The activation energy for the diffusion of Au in Pb is 0.40 eV, which is dominated by Au interstitial diffusion, and has been shown[9] to apply (no observable curvature in the Arrhenius line) over the temperature range 333 – 573 K. Quenching of vacancies in lead[30] ($E_m \cong 0.5$eV) at rates of $(1-3)\times 10^4$ K s^{-1} showed signs of vacancy loss for quench temperatures over 450 K. However, those gold atoms residing in substitutional sites[4,8,9] would be retained more completely because of their lower mobility. Decker *et al.*[9] suggest that in a *Pb*Au alloy containing 500 at. ppm Au, ~80% of the gold would be on substitutional sites. We cannot, however, exclude that small Au clusters can be formed during the quench. Interestingly the aging of the alloys at 60 °C had only a relatively small influence on the recovery spectrum, since all peaks except II a occur both in the Q and $Q+A$ state.

Although an assignment of unique defect reactions to the different annealing stages is not possible at present, an assigment of a recovery stage to freely migrating defects annihilating at sinks, which have been produced by the irradiation together with the mobile defects, should be possible by the study of the dose dependence of the recovery. Any systematic shift of an annealing stage to lower temperatures with increasing dose indicates that the mean number of jumps during the lifetime of the reacting defects is reduced by an increasing number of radiation-induced sinks. Within the experimental uncertainty, stage III b in both dilute *Pb*Au alloys and pure Pb shows the same dependence on dose. It has been assigned to vacancy migration in pure Pb.[28] Therefore is is reasonable to assign vacancy migration to stage III b also in case of the dilute *Pb*Au alloys.

Of all peaks in stage II, only stage II c″ shifts to lower temperatures with increasing recovery in this stage, indicating the migration of an impurity-interstitial complex. This complex should be small because the magnitude of stage II c″ decreases with increasing Au concentration and with increasing dose and the dose is equivalent to the average number of interstitials per trap. It is therefore suggestive to assign stage II c″ to the migration of a mixed dumbbell. Model calculations[20] have shown the mixed dumbbell to have a high binding energy and to be mobile. The mixed dumbbell is formed when a migrating lead self-interstitial is trapped at a single substitutional Au atom. However, further studies of the annealing kinetics are necessary to verify this interpretation. Stage II c″ anneals at 80 – 90 K suggesting that the migration energy of the mixed dumbbell would be ~0.25 eV, which is lower than the activation energy (0.40 eV) for the diffusion of Au in Pb. However, the activation energy for diffusion would be the sum of the migration energy and the energy to form the Au-Pb diplon from the Au in the substitutional site. Vanfleet[10] calculated the formation enregy of a Au-Pb diplon to be 0.09 eV. If the stage II c″ defect were irradiation at low temperatures would yield an activation energy of ~0.25 eV. The diffusion-anneal temperatures, gold concentrations, and irradiation dose could then be varied to separate the contributions from interstitials, substitutionals, and substitutional dimers.

VI. CONCLUSIONS

Although the present experiments found annealing stages which were dependent on the Au impurity, it was not possible to relate any of these stages uniquely to the formation of a Au-Pb diplon. The possible association of stage II c″ with a Au-Pb diplon suggests that an investigation of the diffusion of Au in Pb at low temperatures under irradiation would be of interest.

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