PHYSICAL REVIEW B VOLUME 20, NUMBER 2 15 JULY 1979

Calorimetric study of stage-I self-interstitial-atom interaction energies in platinum

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(Received 18 January 1979)

The release of stored energy and the change in resistivity in platinum irradiated below 12 K with 16-MeV deuterons were measured continuously during anneals to the end of Stage I at 35 K. The ratio of the rate of energy release to the rate of resistivity recovery was found to increase markedly toward the end of the anneals. This increase is attributed to interactions between self-interstitial atoms which prevent the reactants from reaching vacancies below 35 K. An interaction energy of 0.75 eV/event was derived from the data. This energy may be interpreted as either the pair binding energy or the difference in energy between the interstitial configurations present before and after the interaction.

I. INTRODUCTION

During uncorrelated annealing at low temperatures in face-centered-cubic metals not all mobile self-interstitial atoms (SIA's) recombine with vacancies, even when the concentration of Frenkel pairs far exceeds the concentration of extrinsic traps (impurities) for SIA's. It has long been recognized that under such conditions interactions among SIA's provide the principal mechanisms for immobilizing these defects.[1] More recent work has indicated that in some metals SIA pairs are formed late in Stage I, that these pairs are stable against breakup and become mobile at relatively low temperatures, and that large agglomerates of interstitials may be formed in Stage II.[2,3] Studies of annealing suggest that the interaction radius of one SIA with another is comparable to that for SIA-vacancy recombination[4,5]; and computer simulations suggest that the pair binding energy E_B is quite large, of the order of an electron volt[6,7]; but there have been no experimental determinations of this quantity. The stability of an SIA pair against thermal breakup requires, at the end of Stage I in platinum, a binding energy of only 0.03 eV.

An alternative view which also explains the data from Stage I is provided by the conversion-two-interstitial model.[8,9] In this model the SIA configuration mobile in Stage I is metastable; by interaction with other SIA's it is converted into the stable configuration that first becomes mobile in Stage III. Conversion can also occur by thermal activation and recent experiments based on irradiations at temperatures corresponding to recovery Stages II and III have been interpreted as establishing the barrier to conversion at about 0.22 eV in platinum.[10] There are no data for the energy difference between the metastable and stable configurations, E_C; but it must be appreciably greater than the barrier to conversion, even above 300 K back conversion is negligible.

The present results can be fit into the framework of either model. The energy released by interactions between SIA's in Stage I will be denoted as E_I and can be interpreted as either E_B or E_C, or even as some average of these energies. The resistivity change resulting from the interaction ρ_I has a similar interpretation.

Should the ratio E_I/ρ_I be significantly different from the ratio of the energy released in the recombination of a Frankel pair E_{FP} to the decrease in resistivity upon such a recombination ρ_{FP}, then a properly designed experiment should determine E_I/ρ_I reasonably accurately even against the background of pair recombinations occurring at the same time. Further, if the ratio of SIA interactions to pair recombinations can be calculated, especially if this ratio can be changed in a known fashion, then both E_I and ρ_I can be determined separately. A value near 9.5×10^{-6} Ω cm/at.% has been found for ρ_{FP} in platinum.[11] Theory predicts that E_{FP} should be perhaps four times the formation energy of a vacancy,[12–14] about 1.5 eV in platinum[15,16]; and experiments suggest that this is an overestimate.[17] As mentioned above E_I is expected to be at least $0.1E_{\text{FP}}$ while recovery studies indicate that ρ_I must be very small, perhaps $0.05\rho_{\text{FP}}$ or less in fcc metals.[4,5]

In an earlier paper we discussed briefly the relation between the fate of the SIA's which are mobile in Stage I and the ratio of energy loss to resistivity change.[18] Although both the specimen resistance and the rate of energy release were measured continuously in that work, the resistance measurements during the anneal were not corrected for deviations from Matthiessen's rule and only the integrated values over the entire anneal of energy release and resistivity change were computed. The small changes in the integrated ratio $(1/m)(\Delta E/\Delta\rho)$, where m is the specimen mass, were ascribed to the nonadditivity of the resistivity increments resulting from defects present before the irradiation and from Frenkel defects injected during the irradiation and removed during the anneal. Schilling has also commented on the relative insensitivity of $(1/m)(\Delta E/\Delta\rho)$ to the type of irradiation or to the concentration of prequenched vacancies,[17] both of which drastically affect the disposition of SIA's during the anneal. One reason for this insensitivity should be that pair recombination proceeds throughout Stage I in pure metals while interactions between SIA's become important only in the latter part of this stage. Instantaneous values of the ratio $(1/m)(dE/d\rho)$ should be measured throughout the anneal to avoid submerging the desired information in an average that includes a long interval in which the only operating interaction is pair recombination.

No studies have been published in which continuous measurements of both energy release and resistivity decrease were made during an anneal. Low-temperature calorimetric measurements are often continuous but generally the specimens used in such work have poor geometry for resistance measurements; so that at best only the total resistance change over the complete anneal is determined. In addition to our earlier work on irradiated platinum[18,19] continuous measurements of resistivity were made during one set of studies on energy release in nickel[20]; but again only the integrated values of total energy release and total resistivity change to the end of Stage I were published.

We have developed a calorimetric technique based on differential power analysis (DPA) which is well suited to the use of specimens having good geometry for resistance measurements.[19,21] The current through the specimen and the voltage drops across it are measured frequently as the specimen heats adiabatically giving both its instantaneous heat capacity and resistance. The present paper describes the application of this technique to the study of the energy released during SIA interactions in platinum. Platinum was chosen since it is easy to inject excess vacancies into the specimen by quenching before irradiation. These vacancies increase the fraction of mobile SIA's which recombine. The irradiations were designed to inject Frenkel pair concentrations near the maximum that can be analyzed by DPA, the concentration for which at some temperature the rate of energy release from defect reactions alone is sufficient to heat the specimen above its surroundings. Large defect concentrations increase the relative accuracy of the measurements and provide a means of distinguishing the desired effect from artifacts produced by deviations from Matthiessen's rule.

II. EXPERIMENTAL DETAILS AND RESULTS

The irradiation calorimeter is shown in Fig. 1. The irradiation cup is bolted to the bottom of the center tube in a commercial, gas flow cryostat (Andonian Associates, Waltham, Mass.) Liquid helium from the cryostat reservoir flows through a capillary tube into the bottom of the cup at a rate governed by a remote controlled needle valve. Spent helium gas exhausts through a manifold at the top of the cryostat. The inner chamber contains helium gas at atmospheric pressure during irradiations and is evacuated to better than 10^{-6} Torr during anneals. Stainless-steel foils 2.5×10^{-3} cm thick are soldered leak tight over the apertures in the brass irradiation cup and the stainless-steel inner chamber. The copper thermal shield around the specimen is bolted in intimate thermal contact with the copper specimen block. Copper foils 1.2×10^{-3} cm thick are soldered over the apertures in this shield.

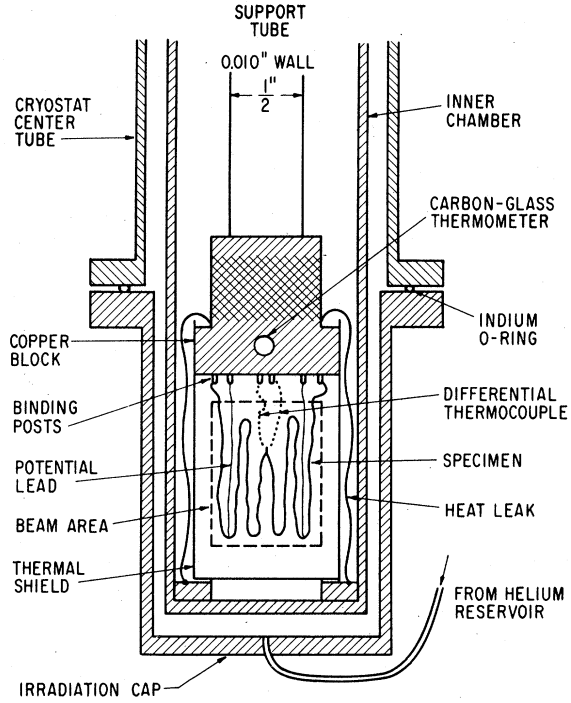

FIG. 1. Specimen and irradiation calorimeter.

The rate of heat removal during irradiation from the specimen in the present arrangement is more than an order of magnitude greater than the rate from a similiarly irradiated specimen in vacuum. This enhanced cooling compared to that in our earlier work[18,19] permitted the accumulation in the available irradiation times of defect concentrations so large that at the temperature of maximum annealing rate the measured specimen specific heat was reduced to less than 30% of its value at that temperature without annealing. In addition, the specimen remained cool enough that recovery substage I*B* could be studied; and almost the entire specimen could be irradiated. This latter feature considerably simplifies the analysis.[19]

The specimen was an 8 inch long, 10×10^{-3} inch diameter, platinum wire (drawn from 99.999% pure stock by Sigmund Cohn. Corp., Mt. Vernon, N. Y.). Three 2×10^{-3} inch diameter leads of the same material were sintered to the specimen. The Au + 0.07 at.% Fe vs chromel differential thermocouple was spotwelded to the $\frac{1}{4}$ inch long central lead and the two others each about $2\frac{1}{2}$ inches from the center served as potential leads. Transition pieces of 16×10^{-3} inch diameter platinum, $\frac{1}{2}$ inch long, were spot-welded to the ends of the specimen and these were soldered to the calorimeter binding posts.

Once mounted the specimen remained attached to the block. Before the first irradiation it was annealed in air by Joule heating at a series of temperatures decreasing from 1700 to 750 K over a period of an hour. Its residual resistivity measured in liquid helium was 2.36×10^{-9} ohm cm. After each irradiation the support tube was withdrawn from the cryostat and the specimen annealed in air for 30 minutes at 1000 K and ten minutes at 750 K. After each such anneal the change in residual resistivity from its previous annealed valve was less than 0.1×10^{-9} ohm cm. For quenches the specimen was heated to 1950 K then immersed in distilled water. After a ten minute anneal at 425 K to reduce the effects of quenching strains, the resistivity increment was measured in liquid helium.

The irradiations were performed with 22.5-MeV deuterons from the Argonne National Laboratory cyclotron. The mean deuteron energy in the specimen, after losses in isolating foils and the exchange gas was 15.8 MeV.[22] The specimen resistance, the block temperature, and the thermocouple output were monitored continuously during irradiations and the deuteron current was adjusted so that the entire specimen remained below 11 K. The beam current density did not exceed 17×10^{-9} A/cm^2. Since the average deuteron loses nearly half of its incident energy in traversing the specimen damage production is inhomogeneous. To partially compensate for this spatial difference in displacement rates the specimen holder was rotated 180° half way through each irradiation. A comparatively thick specimen was used so the magnitude of the stored energy would be as large as practicable.

In the cryostat the residual resistance of the specimen is measured at 4.50 K with exchange gas in the chamber. This temperature, determined by the carbon-glass thermometer, could be accurately held with small power on the heater and the measured resistivity was reproducible to within 2×10^{-11} ohm cm.

After each irradiation the inner chamber was evacuated then anneals to determine energy release were carried out as described in Ref. 19, with the exception that here data processing was initiated by the first temperature reading above 12 K. With minor changes the circuitry is the same as that of the earlier work.[19]

Since almost the entire length of the specimen was irradiated it was unnecessary to correct for longitudinal heat flow resulting from the higher rate of energy generation in the irradiated as compared to that in the unirradiated sections.[19] With this simplification the measured power required to heat the specimen through each $\frac{1}{4}$ K interval was plotted for each anneal and for each subsequent heat without recovery. The differences between each such pair were connected by smooth curves, corrected for thermoelectric effects as described below, and plotted as in Fig. 2.

The extent of recovery substages I*B* and I*C*, defined as the first two intervals between minima in the energy release spectra, and the percentage recovery are indicated on this figure. The percentage recovery is $100(1-\Delta\rho/\Delta\rho_0)$ where $\Delta\rho$ is the resistivity increment (converted to 4.2 K) above the preirradiation value and $\Delta\rho_0$ is the resistivity that would have been injected into an annealed specimen at 4.2 K by the irradiation. For the present irradiations $\Delta\rho_0$ is computed by dividing the resistivity increment measured after the 12 K anneal by 0.96; numerous measurements have shown that 4% of the resistivity injected at 4.2 K by irradiations such as these recovers in substage I*A*. Since an identical irradiation injects a greater resistivity increment into quenched than into annealed platinum[23,24] this procedure produces initial values of $\Delta\rho/\Delta\rho_0 \equiv Y$ that are greater than unity in quenched specimens. However for equivalent fluences equal values of Y represent equal defect concentrations regardless of quench enhanced defect injection.

The difference in resistance between a specimen

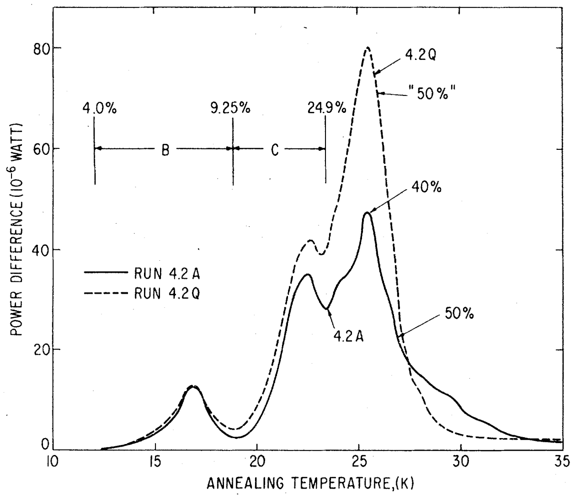

FIG. 2. Energy release as a function of annealing temperature of platinum irradiated as annealed (4.2*A*) and after quenching (4.2*Q*).

containing self-interstitials and vacancies and the same specimen without these defects is a function of the measurement temperature. The resistances given by the data acquisition program must be corrected for this temperature dependence of the defect resistivity (deviation from Matthiessen's rule). The corrections were determined in subsidiary experiments.[25] The results are plotted in Fig. 3 and are used to convert the rate of resistance change measured at any annealing temperature to the equivalent resistivity annealing rate that would have been measured at 4.2 K. The latter is closely proportional to the rate at which Frenkel pairs recombine.[19,26]

Much data from our previous studies of energy release in platinum are applicable to the present work. Information on the preparation, irradiation, and recovery of all specimens used in this analysis is compiled in Table I. Each of the four specimens is denoted by a different numeral before the decimal. The present specimen is number four, the others are described in Ref. 18.

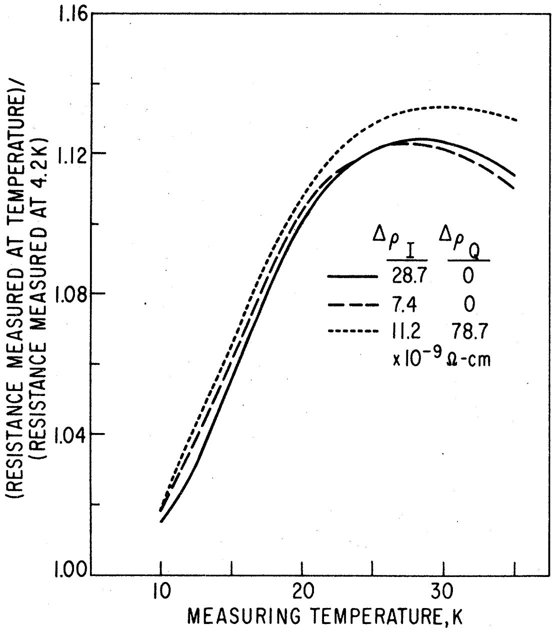

FIG. 3. Temperature dependence of the resistivity increment in platinum due to irradiation.

Recovery was much the same for all annealed specimens in the table; Y at 35 K was always near 0.40, and the several maxima in the annealing rate occurred at similar values of Y (IB near 0.935, IC near 0.80, and ID near 0.60). For these defect concentrations in specimens of the present purity almost all SIA's mobile in Stage I either combine with vacancies created during the irradiation or are immobilized by interactions with other SIA's.[27] With the maxima in dE/dt and in $d\rho/dt$ set at the above values and with the end point at $Y=0.40$ all annealed specimens were treated together in the analysis.

Recovery in quenched specimens depends upon both the irradiation dose and the detailed sink concentration produced by the quench.[23] However, among the specimens from Table I, Y at 35 K was near 0.29 for the two specimens with the smallest

TABLE I. Energy release and resistivity recovery in platinum after deuteron irradiation.

Irradiation	Fluence ($10^{14} d/\text{cm}^2$)	Resistivity Charge (10^{-9} Ω cm) $\Delta\rho_Q$[a]	$\Delta\rho_I$[b]	$\Delta\rho$[c]	Energy Release (10^{-6} J) ΔE[c]	$\Delta E/m\Delta\rho$ (J/g)/10^{-6} Ω cm
1.1Q	8.8	72.8	7.53	5.34	252	2.47
1.1A			6.37	3.62	181	2.61
1.2A	7.0		5.13	2.92	142	2.55
1.2Q		81.1	6.29	4.53	216	2.50
1.3Q	12.0	75.3	9.24	6.71	314	2.45
1.3A			8.52	4.68	231	2.58
2A	10.0		7.20	4.04	214	2.59
3A	10.0		7.14	4.03	202	2.54
4.1A	20.0		18.06	10.26	3572	2.56
4.1Q		95.7	20.97	15.08	5085	2.48
4.2Q	22.5	88.4	23.10	16.39	5572	2.51
4.2A			20.27	11.47	4040	2.59
4.3A	25.0		22.45	12.65	4421	2.57

[a] $\Delta\rho_Q$ is the resistivity added by the quench.

[b] For specimens 1, 2, and 3 $\Delta\rho_I$ is the resistivity increment after irradiation and anneal at 17 K. For specimen 4 $\Delta\rho_I$ is the increment after irradiation and anneal at 12 K.

[c] $\Delta\rho$ and ΔE are the resistivity recovered and the energy released upon heating to 35 K.

doses, 1.1Q and 1.2Q; and was about 0.31 or 0.32 for the two with the largest doses, 4.1Q and 4.2Q. The ratio of resistivity injected by the irradiation to that from the quench for 1.3Q was intermediate to the above pairs; but the enhancement of the damage rate, the damage remaining at the ID maximum, the final value of Y, and the ratio of energy release to resistivity recovery were all anomolously low. The damage rate reduction is characteristic of appreciable plastic deformation before the irradiation.[28]

In Fig. 4 the instantaneous ratio of the rate of energy release to the rate of energy recovery, $(1/m)(dE/d\rho)$, is plotted for specimens which were annealed before irradiation. The data from all A specimens in Table I, weighted by the ratio of ΔE to the specimen cross section, are used for recovery above 17 K ($Y < 0.9$); below that temperature only data from the present series were available.

The cross hatched region in Fig. 4 extends one standard deviation to either side of the mean value of $(1/m)(dE/d\rho)$. The relative scatter in energy release is large in the IB region since the control parameter, the temperature different between the block and the center of the specimen with zero power applied to the specimen, is small at low temperatures where the thermal diffusivity is very high. The scatter in resistivity is greatest at the highest temperatures. The thermometer sensitivity decreases and the accumulated thermocouple drift and, most importantly, the temperature coefficient of resistiviy of the specimen increase with temperature. Based on successive heats of unirradiated specimens the reproducibility of resistivity measurements is 5×10^{-11} Ω cm at 15 K, 1×10^{-10} Ω cm at 25 K, and 2×10^{-10} Ω cm at 35 K.

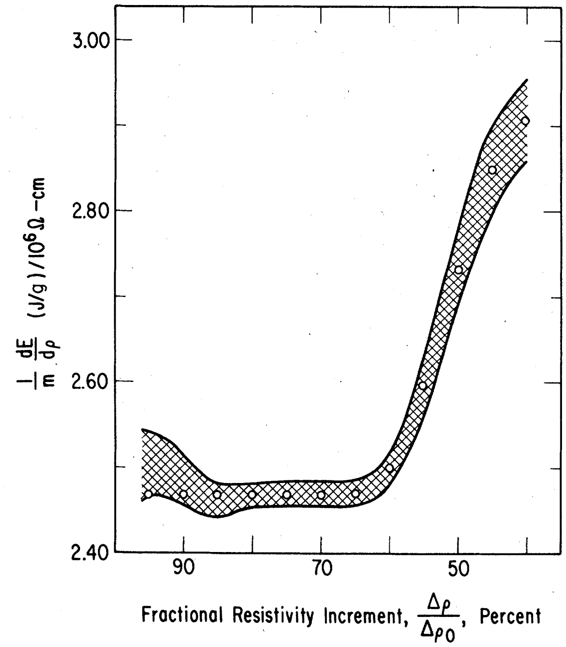

FIG. 4. Instantaneous ratio of energy release to resistivity recovery after irradiation of annealed platinum. Data from all specimens are used.

The values of $(1/m)(dE/d\rho)$ for the quenched specimens are listed in Table II. From the beginning of the anneals into the early part of substage ID, i.e., for $Y > 0.65$, the average value of this ratio in each quenched specimen except 1.3Q is not significantly different from 2.47 (J/g)/10^{-6} Ω cm, the average value for annealed specimens in the same interval. As recovery proceeds $(1/m)(dE/d\rho)$ in quenched specimens systematically deviates from its value in annealed ones. In particular this ratio increases less in quenched platinum and, unlike the annealed speci-

TABLE II. Average values of $(1/m)(dE/d\rho)$ in selected annealing intervals.

	Annealed Specimens	Specimens 4.1Q 4.2Q		Specimens 1.1Q 1.2Q	
	Expt[a]	expt[a]	Calc[b]	Expt[a]	Calc[b]
$\Delta\rho/\Delta\rho_0$	(J/g)/10^{-6} Ω cm	(J/g)/10^{-6} Ω cm		(J/g)/10^{-6} Ω cm	
0.80–0.65	2.47	2.46	2.47	2.47	2.47
0.65–0.60	2.49	2.47	2.47	2.46	2.47
0.60–0.55	2.54	2.49	2.48	2.48	2.48
0.55–0.50	2.66	2.50	2.50	2.50	2.48
0.50–0.45	2.79	2.53	2.53	2.49	2.49
0.45–0.40	2.90	2.55	2.54	2.52	2.50
0.40–0.35		2.55	2.55	2.48	2.49
<0.35		2.53	2.54	2.49	2.49

[a] Expt values are those measured in this work.

[b] Calc values are computed using the parameters derived in the text.

mens, appears to pass through a maximum before the end of Stage I.

The largest source of systematic error arises from thermal voltages generated in the thermocouple circuit. Precautions were taken to minimize these stray voltages[19]; and a correction for residual drift was calculated based on the observation that between 33 and 35 K the energy release was nearly constant and always very small compared to the energy required to heat the specimen between those temperatures. For annealed specimens the ratio of the measured energy release to the energy required to heat from 33 to 35 K divided by $\Delta\rho_0$ was $0.37/\mu\Omega\,\mathrm{cm}$. (At 25 K it was $15.5/\mu\Omega\,\mathrm{cm}$). For quenched specimens it was this factor divided by the enhancement of $\Delta\rho_0$. Accordingly the power difference at 34 K between each energy release anneal and subsequent heat was corrected to this value and the corrections for other temperatures decreased linearly from the magnitude of the 34 K correction to zero at 12 K in the present anneals, or to zero at 17 K in those performed earlier. The largest correction to the present data was 50×10^{-6} J. The method of compensation in our earlier work[18,19] neglected the change during recovery of the ratio $(1/m)(dE/d\rho)$; the entries for these irradiations in Table I and Table II of this paper include the compensation described above.

There was no evidence of significant changes in measured specific heat due to gas reactions on the specimen surface. This is different from the observation of Feese and co-workers who reported a continuous background exothermic reaction, the rate of which increased monotonically with annealing temperature; and which they ascribed to a surface effect resulting from the irradiation of adsorbed gas molecules.[29] The ratio of irradiated volume to specimen surface area was considerably more than an order of magnitude greater and the irradiating fluences were two orders of magnitude less in the present study than in their work.

III. DISCUSSION

When n reactions with specific energy release E_i and specific resistivity change of ρ_i occur simultaneously with probability X_i; then the instantaneous ratio of energy release to resistivity change is

$$\frac{1}{m}\frac{dE}{d\rho}=\frac{1}{m}\left(\sum_{i=1}^{n}X_iE_i\Big/\sum_{i=1}^{n}X_i\rho_i\right)\ , \tag{1}$$

with the subsidiary condition

$$\sum_{i=1}^{n}X_i=1\ . \tag{2}$$

In the present discussion n will be restricted to two. One reaction with probability X_1 [(i)] is Frenkel pair recombination; the second with probability X_2 [(ii)] is the interaction between SIA's that prevents the defects from taking part in reaction (i).

An additional approximation made only in computing X_1 and X_2 is the assumption that $\Delta\rho$ is proportional to the concentration of SIA's regardless of their configuration. Other recovery studies[5] and the results of the present work show that $\Delta\rho_2 << \rho_{F\rho}$ and since directly produced immobile SIA's are otherwise indistinguishable from those resulting from SIA interactions during annealing this approximation should introduce little error.

During irradiations of platinum at 35 K the instantaneous concentration of mobile SIA's is so small that interactions among these defects are suppressed. If the specimen is quenched so that the concentration of vacancies greatly exceeds the concentration of effective traps almost all mobile SIA's combine with vacancies. Extrapolating to zero fluence the data from resistivity measurements during irradiations with 20-MeV deuterons of platinum quenched as in the present work yields, at $\Delta\rho_0=0$, a rate of resistivity increase about 27% of the rate in annealed platinum irradiated at 6 K.[30] For irradiations to finite doses of platinum quenched as in the present work Y at 35 K increases from near 0.27 for $\Delta\rho_0<2\times10^{-9}\ \Omega\,\mathrm{cm}$ to near 0.35 for $\Delta\rho_0\sim150\times10^{-9}\ \Omega\,\mathrm{cm}$.[23]

The data plotted in Fig. 4 show that the ratio of energy release to resistivity recovery does not change significantly until annealing has proceeded into substage I*D*. At lower annealing temperatures corresponding to $Y>0.65$, recovery consists of the recombination of close Frenkel pairs, those for which the first SIA jump is biased toward a vacancy, in substage I*B* and I*C*[25]; and of unbiased but spatially correlated Frenkel pairs which recombine in very few jumps in the early part of I*D*. The data in Fig. 4 show that the ratio X_2/X_1 does not change for $0.9>Y>0.65$ which, since the rate of recombination fluctuates greatly, strongly implies that X_2 is very near zero throughout the interval.

Current models of the structure[31] and the dimensions[32] of displacement cascades also predict that almost no type (ii) interactions occur during the very few SIA jumps required to anneal to $Y=0.65$. Experimentally almost no SIA clusters are observed unless either the dose is so large that there is extensive cascade overlap[33] or that the temperature is high enough for extensive SIA diffusion.[31] In the present irradiations $\Delta\rho_0$ is always less than one percent of the saturation resistivity in platinum[24] and the rate of resistivity increase in annealed specimens falls by only a few percent below the rate given by an extrapolation to zero fluence.[34]

Accordingly, we take for the reaction probabilities

$$X_2=0\quad\text{for } Y>0.65 \tag{3}$$

and

$$\int_{0.65}^{Y_F} X_1\,dy = \frac{0.65 - Y_F}{0.65 - 0.27} \quad . \tag{4}$$

In Eq. (4) Y_F is $\Delta\rho/\Delta\rho_0$ at 35 K. As annealing proceeds X_1 should decrease from the value unity characteristic of completely correlated recombinations toward a value characteristic of a random distribution of SIA's and vacancies. This latter value X_{1R} is given by

$$X_{1R} = \frac{R_v C_v}{R_2 C_2 + R_v C_v} \quad . \tag{5}$$

In the expression R_v and R_2 are the interaction radii for type (i) and type (ii) interactions, C_v is the concentration of vacancies, and C_2 is the concentration of complexes at which type (ii) interactions occur. Due to clustering in general $C_v > C_2$. The solid line drawn in Fig. 5 satisfies Eqs. (3) and (4) for annealed platinum ($Y_F = 0.40$).

The data in Table II show that in quenched specimens not only does $(1/m)(dE/d\rho)$ increase far less than what it does in annealed specimens but also that it passes through a maximum before the end of the anneal. This means that X_2 must decrease at the smallest values of Y. This behavior is sketched in Fig. 5 for the appropriate specimens. Physically this occurs because the concentration of complexes that a mobile SIA can interact with decreases far more rapidly than does the concentration of vacancies. For the lower dose quenched specimens the vacancy concentration decreases by less than 3% and the concentration of complexes for type (ii) interactions decreases by more than a factor of 2 while annealing through values of Y for which $X_2 > 0$. Toward the end of the anneal the only type (ii) interactions are between the few remaining mobile SIA's and those SIA's originally produced in immobile configurations. The maxima in X_2 result from a combination of this decreasing relative concentration of X_2 reactants and the increasing lack of correlation in the SIA-vacancy distribution as the anneal proceeds.

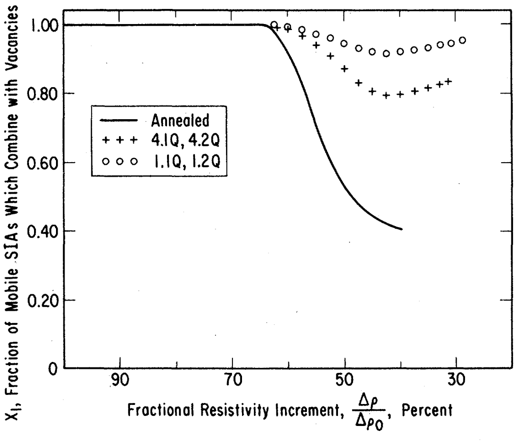

FIG. 5. Instantaneous ratio of the pair-recombination rate to the total self-interstitial-atom reaction rate.

The ratio of energy release to resistivity recovery, 2.467 ± 0.016 (J/g)/10^{-6} Ω cm, derived from the data for all specimens, except $1.3Q$, in substage IC and the early part of ID must be interpreted as $(1/m)(dE_{\rm FP}/d\rho_{{\rm F}_\rho})$. Combining this ratio with the value of the Frenkel pair resistivity given in Ref. 11, $(9.5 \pm 0.5) \times 10^{-6}$ Ω cm/at.%, yields 4.7 ± 0.3 eV for the energy given up in the recombination of a Frenkel pair.

Permissable values of E_2 and ρ_2 are limited to the set which, when coupled with physically reasonable values of X_2 that satisfy Eqs. (3) and (4), reproduce the ratios of energy release to resistivity recovery plotted in Fig. 4 and listed in Table II. These requirements mean that E_2 and ρ_2 are strongly correlated. The best fits to the centroids of the data are given by

$$E_2 = 0.75 \text{ eV}, \quad \rho_2 = 0.25 \times 10^{-6} \ \Omega \text{ cm/at.\%} \quad .$$

Ratios calculated with this set and the solid curve in Fig. 5 are plotted in Fig. 4; ratios for the quenched specimens calculated using the corresponding X_1 vs Y curves from Fig. 5 are listed in Table II. The maximum value of E_2 for which a satisfactory fit to all the data can be achieved is 1.0 eV with an accompanying ρ_2 of 7×10^{-7} Ω cm/at.%; for larger values the rate of increase of $(1/m)(dE/d\rho)$ with increasing X_2 is too small to fit both the quenched and the annealed specimens. Similarly the smallest value of E_2 is 0.45 eV accompanied by a ρ_2 of -0.1×10^{-6} Ω cm/at.% (the negative value of ρ_2 corresponds to a resistivity increase from the reaction); for smaller values $(1/m)(dE/d\rho)$ rises too quickly as X_2 increases.

At the lowest annealing temperatures corresponding to recovery substage IB, the observed values of $(1/m)(dE/d\rho)$ are generally higher than the value attributed above to $(1/m)(dE_{\rm FP}/d\rho_{\rm FP})$. This increase must result from changes in $E_{\rm FP}$ or $\rho_{\rm FP}$. Since $E_{\rm FP}$ for a Frenkel pair in which the first jump of the SIA is biased toward the vacancy should not be higher than $E_{\rm FP}$ for a vacancy and an uncorrelated SIA, the increase in $(1/m)(dE/d\rho)$ must be ascribed to a small reduction in $\rho_{\rm FP}$ for the IB pairs.

The present model accounts for the differences in $(1/m)(dE/d\rho)$ between quenched and annealed specimens in terms of the fraction of SIA's that recombine with vacancies; it is not necessary to propose that the resistivity increments due to Frenkel pairs and to vacancies from the quench are not additive at 4.2 K. Since all irradiations give the same value of $(1/m)(dE/d\rho)$ when only pair recombination occurs, whether or not vacancies are present, deviations from additivity at 4.2 K must be less than $0.005\Delta\rho$.

After a type (ii) reaction, most of the SIA formation energy is stored in the strain fields associated with the new configuration. With the present technique and using specimens irradiated to near saturation it should be possible to study the complete release of this energy on annealing to about 500 K. The average rate of energy release should be comparable to the rates measured in this work, although the background lattice specific heat is much higher and considerably more care must be taken to insure adiabatic conditions than at low temperature,[21] but measurements of the requisite sensitivity have been made in a previous investigation.[35]

From $Y = 0.65$ to the end of the anneal at $Y = Y_F$, the interval in which type (ii) reactions occur, in each quenched specimen the average value of X_2/X_1 given by

$$\frac{\bar{X}_2}{\bar{X}_1} = \frac{Y_F - 0.27}{0.65 - Y_F} \tag{6}$$

is more than double the average SIA concentration divided by the average vacancy concentration. In annealed specimens for which the concentrations of SIA's and of vacancies are always the same $\bar{X}_2/\bar{X}_1$ is about 0.5 and even the maximum value of X_2/X_1, which should approach R_2/R_v, is near 1.5. This greater than random probability in quenched specimens for interactions between SIA's as compared to SIA-vacancy recombinations despite the simultaneous occurrence of some correlated Frenkel pair recombinations is a consequence of the nonhomogeneity of defect production during irradiations with ions. The mean primary knock-on energy in the present irradiations is about eight times the average displacement energy. Most defects are produced in cascades where the local ratio of Frenkel pairs to quenched-in vacancies is greater than an average over the specimen. The sites of the low-energy displacements are also correlated with the path of the deuteron.

IV. CONCLUSIONS

The average energy released per event in interactions among SIA's which prevent the reactants from combining with vacancies during Stage I recovery is 0.75 ± 0.25 eV.

The average resistivity change associated with these interactions lies between a decrease of 0.7×10^{-6} Ω cm/at.% and an increase of 0.1×10^{-6} Ω cm/at.%.

Changes in electrical resistivity measured at 4.2 K are, to within one percent, proportional to changes in the Frenkel pair concentration, even in the presence of a much greater concentration of vacancies injected by a prior quench.

ACKNOWLEDGMENTS

The author is indebted to E. A. Ryan who devised this calorimetric technique and who gave valuable assistance in programming the data acquisition system. He also thanks M. Oselka under whose direction the many irradiations with carefully controlled beams were performed. Work performed under the auspices of the U.S. DOE.

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