Low-temperature energy release in platinum after ion radiation*

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The release of stored energy and the change of resistivity were measured simultaneously in the same specimen during the annealing from 15 to 35 K of platinum irradiated with 20-MeV deuterons. The calorimeter and differential power analysis used are described in detail. The work was undertaken to determine whether the enhanced initial rate of resistivity increase during the irradiation of quenched platinum, as compared to the rate in annealed platinum, results from greater Frenkel-pair production or a larger Frenkel resistivity in the quenched material. The results indicate that most of the enhancement in these irradiations represents increased production. The resistivity increment per defect added by the irradiation when measured at 5 K is increased only a few percent by the vacancies from the quench. The additional interstitials are preferentially deposited near these vacancies. Using an estimated energy stored in each Frenkel pair of 6 eV the resistivity increment at 5 K of unit concentration of Frenkel defects in platinum is 12×10^{-4} Ω cm.

I. INTRODUCTION

Electrical resistivity can be measured quickly, precisely, and nondestructively; it is the parameter most used to monitor small changes in defect concentration during irradiation and annealing. However, resistivity suffers from two drawbacks. First, it is not specific to the type of defects present and thus is not very sensitive to reactions that change the composition of the defect population. Examples of such reactions are the agglomeration of mobile defects into immobile clusters and the trapping of mobile defects at immobile ones. Second, the relation between changes in resistivity and changes in defect concentration is not always known even when the composition of the changing concentration remains the same. This is the subject of the present paper. A well-studied example is provided by radiation damage in very thin metal specimens.[1,2] If the defect concentration increases at the same rate in a bulk specimen and a second specimen, otherwise identical, but with one dimension smaller than the electron mean free path, then the initial rate of resistivity increase in the thin specimen is greater than that in the bulk one; but with increasing dose the rate in the thin one approaches that in the bulk specimen.

The ratio of the rate of resistivity increase during low-temperature irradiation in many, but not all, imperfect lattices to the rate in more nearly perfect lattices is qualitatively similar to that described above.[3] Indeed, thinness may be considered as a form of lattice imperfection. One of the most studied imperfect systems is quenched platinum, a supersaturated substitutional alloy of vacancies in an otherwise nearly perfect lattice. Enhancements of the initial rates of resistivity increase in quenched specimens up to 30% greater than the initial rates in annealed but otherwise identical specimens have been reported for neutron or ion irradiations[4,5]; the enhancements are much smaller for near-threshold electron irradiations.[6] The enhancement increases monotonically with quenched-in vacancy concentration. The rate of resistivity increase falls more rapidly with dose in quenched than in annealed specimens so that at Frenkel-pair concentrations greater than 5×10^{-5} the rates have become nearly independent of the preirradiation treatment.

Two explanations have been proposed for these observations. One asserts that the enhancements of resistivity in quenched platinum and in other imperfect lattices are consequences of deviations from Matthiessen's rule, i.e., that the resistivity increment resulting from defects injected before irradiation and those injected by the irradiation is greater than the sum of the specific resistivities of each of the two types of defects.[7] The other proposes that the enhancement arises primarily from a greater production of Frenkel pairs in imperfect lattices; these result from the scattering of focused replacement collision sequences in the strain fields of the defects present before irradiation.[8]

To determine which explanation is more nearly correct it is necessary to compare the change in residual resistivity with the change in some other observable, one that has a known relation to the change in the number of defects. This second observable will be referred to as a fundamental observable. The ratio of the change in resistivity to that in the fundamental observable must be determined to within an accuracy of a few percent both in quenched specimens and in specimens annealed before irradiation. Because of the saturation of the enhancement with dose it is also necessary that the maximum Frenkel-pair concentration be of order 10^{-5}. In this dose range there are many ob-

servables the changes in which should be closely proportional to changes in defect concentration, but scarcely any of them can be measured with the requisite precision. The discussion of Ref. 9, for example, shows that even refined x-ray lattice-parameter measurements are not useful in the present problem. Recently, sufficiently precise measurements of changes in elastic constants during irradiation have been published,[10] but these require samples too massive for efficient quenching or irradiation with charged particles.

The great precision possible in the measurement of residual electrical resistivity in pure metals is largely due to its low background, the low resistivity near 0 K of defect-free specimens. Specific heat is another observable that has a similarly low background; this property has been utilized in measurements of energy release at low temperature.[11-15] Since the activation energy of uncorrelated interstitial diffusion in stage I is expected to be two orders of magnitude less than the energy released by the recombination of a Frenkel pair in platinum,[14,16] all stage-I recovery processes should release nearly the same energy per recombination irrespective of the presence of other defects in the lattice. Thus, the change in specific heat is a fundamental observable for those defects which recover in stage I; but in applying the results of such measurements to the present problem one must take into consideration that not all of the defects which contribute to the charge in residual resistivity recover in stage I.[17]

A technique developed in this laboratory to measure changes in specific heat resulting from defect recovery above room temperature is sufficiently sensitive to make the required measurements.[18,19] In addition, the technique is designed specifically to use the small specimens required for quenching and for irradiation with ions. This technique is compared with more standard calorimetric techniques in Sec. II. After that the method is described in detail and the results presented. This is followed by a discussion of the implications of these measurements to radiation effects.

II. CALORIMETRY

In most calorimetric studies at low temperature the rate of energy release is calculated from the difference in specimen heating rates between a run in which defect recovery takes place and a subsequent run with no recovery.[11-14] However, this technique, differential thermal analysis (DTA), has certain drawbacks which reduce its usefulness for an investigation of differences in energy release among specimens with small concentrations of Frenkel pairs. Since DTA specimens cannot be adiabatic, temperature increases due to energy release are diminished by heat flow from the specimen. The rapid increase of specific heat with temperature in stage I acts as a virtual heat leak which also reduces the effect of energy release on specimen temperature. Accurate subsidiary measurements of both the losses from and the specific heat of the specimen are needed to determine energy release from the measured heating rates. A drawback to DTA particularly relevant to this investigation arises from changes in the specimen specific heat due to the presence of defects[20]; this would require that the specific heat of annealed and of all quenched specimens be known throughout the recovery interval.

To avoid these drawbacks and to minimize damping of the observable effects of energy release by heat flow from the specimen, the measurements presented here were made by differential power analysis (DPA). This technique has been highly developed by Clarebrough and co-workers for calorimetric measurement above room temperature in massive deformed specimens,[21] and has been used to measure the effects of impurities on the ratio of energy release to resistivity recovery during stage-I annealing of nickel.[15] For DPA the specimens are mounted within an isothermal shield which is heated at a reproducible rate. The specimens are heated independently and the power required to keep them at the temperature of the shield is measured. Ideally the full magnitude of the energy release is given directly by the difference between the external power required to heat the specimen when recovery takes place and that required in a subsequent heat when no defects anneal. The main experimental problem in the application of DPA to stage I annealing arises from the very large thermal diffusivities of pure metals at low temperatures. This reduces the control parameter, the temperature difference between shield and specimen with zero power applied to the specimen heater. As compensation another consequence of the small specific heat in stage I is that the expected maximum rate of energy release due to recombination of the small Frenkel-pair concentrations in the present work should reduce the external power needed to heat the specimen by about 10%.

III. SPECIMEN PREPARATION, IRRADIATION, AND RECOVERY

The irradiation calorimeter and specimen arrangement are shown in Fig. 1. The specimen itself serves also as heater and support so that parasitic masses are minimized. Since heat flow from the specimen by conduction through residual

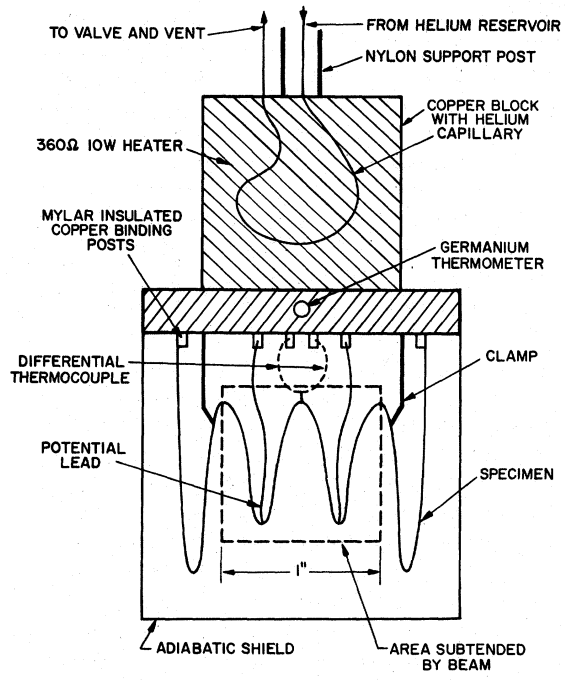

FIG. 1. Specimen and irradiation calorimeter.

gases and by radiation is negligible, in effect the surrounding shield is reduced to the base plate where the specimen is attached. Radiative heat transfer is minimized by surrounding the specimen with a thin aluminum foil in thermal contact with the base. The calorimeter is bolted to the controlled temperature stage of a commercial cryostat (Cryogenics Associates, Indianapolis, Ind., Model-Versastat). The stage can be cycled between 4.5 and 310 K with control better than $\pm 1\times10^{-2}$ K in the region of interest. The calorimeter is enclosed in a liquid-nitrogen-cooled shield which has two holes covered by 5×10^{-4}-in.-thick aluminum foil for passage of the deuteron beam.

The specimen was 6×10^{-3}-in.-diam platinum wire drawn in this laboratory from nominally 99.999% pure 10×10^{-3}-in.-diam wire (supplied by Sigmund Cohn Corp., Mt. Vernon, N.Y.). Three 2×10^{-3}-in.-diam wires of the same material were sintered to the specimen at 1-in. intervals. The outer two wires served as potential leads and the central stub was the point of attachment of the Au+0.07-at.%-Fe–vs–chromel differential thermocouple. The resistivity measured at 4.2 K of the specimen after preparation and anneal was 2.91×10^{-9} Ω cm.

The specimen to be quenched was suspended horizontally just above a bath of distilled water in a large cylinder. It was heated by direct current through clamps well outside the potential leads. Quench temperatures were near 1900 K. During the quench the specimen remained stationary and was submerged by raising the cylinder. The resistivities added by the quenches were determined from the change in resistance measured at 4.2 K and are shown in Table I.

Connections to the specimen in the cryostat were made through indium plated copper binding posts. These posts were electrically insulated from the base by 2.5×10^{-4}-in.-thick Mylar sheets. After mounting, quenched specimens were annealed for 10 min at 425K to reduce the effects of possible strains from handling and annealed specimens were further annealed for 5 min at 800 K. Upon cooling the block and specimen to 5 K the preirradiation resistance is measured. Relay-operated clamps are then closed just outside the portion of the specimen in the beam. These rhodium plated copper clamps improve thermal contact between specimen and block and are opened after the irradiation is completed.

The irradiations were performed with 22.5-MeV deuterons from the Argonne National Laboratory 60-in. cyclotron. The mean deuteron energy in the specimen was 19.7 MeV. The resistance of the

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

Irradiation	Fluence (10^{14} deuterons/cm^2)	Resistivity change (10^{-9} Ω cm) $\Delta\rho_Q$ [a]	$\Delta\rho_I$ [b]	$\Delta\rho$ [c]	Energy release ΔE (17–35 K) (10^{-6} J)	$\Delta E/m\Delta\rho$ J/g / μΩ cm
1Q	8.8	72.82	7.53	5.34	253	248
1A			6.37	3.62	182	263
2A	7.0		5.13	2.92	142	255
2Q		81.06	6.29	4.53	217	250
3Q	12.0	75.27	9.74	6.71	313	244
3A			8.52	4.68	230	257

[a] $\Delta\rho_Q$ is resistivity added by the quench.
[b] $\Delta\rho_I$ is resistivity increment measured at 5 K after irradiation and anneal at 17 K.
[c] $\Delta\rho$ is resistivity removed measured at 5 K after heating to 35 K.

specimen, the temperature of the block, and the output of the differential thermocouple were monitored during irradiation and the deuteron current was adjusted so that no part of the specimen was heated above 15 K. The deuteron current density was always less than 6×10^{-9} A/cm^2.

There were three sets of irradiations. In each set the specimen was irradiated once as quenched and once as annealed. Both irradiations of each set were to the same fluence. Details of the quench and irradiation procedures are given in Table I.

After irradiation the block and specimen are held at 17 K for 5 min then cooled to 5 K for measurement of the resistance increase. The anneal at 17 K removes the defects which recombine in substages IA and IB and produces a defect distribution which does not depend upon the temperature profile during irradiation. The block and specimen are then heated at a programmed rate through the interval 15–35 K while frequent measurements are made of the input power to and resistance of the specimen. Following this run the resistance is again measured at 5 K and measurements of input power and resistance are made during one or more heats at the same rate to 35 K.

IV. MEASUREMENT AND ANALYSIS

A schematic diagram of the measuring and control circuits is shown in Fig. 2. The nonlinear-resistance–vs-temperature characteristic of the germanium sensor is drawn on the control chart of an analog programmer (Data-Trak, model 5500, Research, Inc., Minneapolis, Minn.). The amplified deviation between the programmer and thermometer outputs drives a biased voltage-programmable power supply which supplies the heater on the controlled temperature block. The deviation never exceeds 2×10^{-6} V, which corresponds to ±0.002 K at 15 K and 0.01 K at 35 K. The apparent specimen specific heat is a function of the heating rate.[19]

The amplified output of the differential thermocouple drives a more sophisticated temperature controller (Artronix 5301-E, St. Louis, Mo.) which supplies direct current to the specimen. The additional voltage source in the thermocouple circuit is adjusted so that the correct specific heat of annealed platinum is measured between 15 and 35 K.[22] The current required to heat a loss-free specimen is proportional to $(C_p/\rho)^{1/2}$, where C_p is the specific heat and ρ the resistivity. These quantities are plotted in Fig. 3 which shows that the current is nearly constant during the measurements.

In general the accuracy of energy-release measurements increases with heating rate. Rapid heating is particularly desirable with the present technique since the control parameter increases linearly with rate. In this work the heating rate was limited by the response time of the control circuits. All data were taken while heating at 4 K/min, a rate which gave a control parameter of 8×10^{-6} V at the temperature of maximum energy release and at which the sum of the voltages from the thermocouple and compensator never deviated by more than 1×10^{-7} V (6×10^{-3} K) from null. The amplified deviations were plotted on a recorder and used to correct the measured specimen heating powers. The power required to maintain known temperature differences across the differential thermocouple was measured at several temperatures in separate experiments. Temperature control was usually established by 15 K. If not, the run was terminated and the parameters of the controllers were readjusted. When the temperature reached 35 K the heaters were turned off and the coolant flow was increased manually. In no run did the maximum temperature exceed 35.2 K.

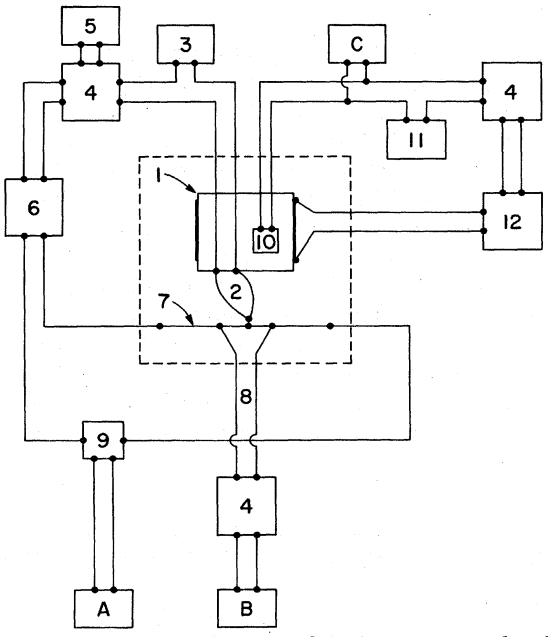

FIG. 2. Schematic diagram of the heating control and measurement circuits. 1, controlled temperature block with heater; 2, differential thermocouple, Au +0.07-at.% Fe vs chromel; 3, adjustable compensating voltage; 4, dc amplifiers; 5, chart recorder; 6, temperature controller and specimen current supply; 7, specimen; 8, specimen potential leads; 9, 1-Ω standard resistor; 10, germanium thermometer; 11, "Data-Trak" curve follower; 12, programmable power supply for block heater; A,B,C, inputs to digital data-acquisition system. The components within the dotted line are located within the volume shown in Fig. 1.

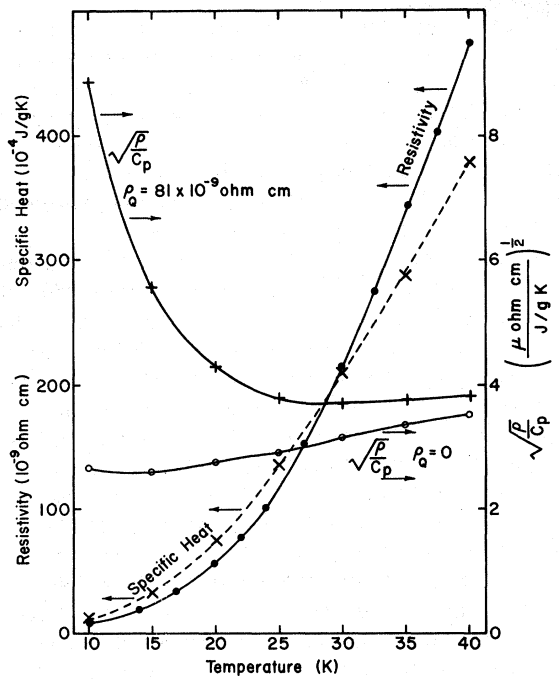

FIG. 3. Specific heat of platinum (Ref. 22), the measured electrical resistivity of the present specimen (annealed), and the ratios of these quantities (quenched and annealed) at the temperatures of the present work.

The temperature, computed from the output of the germanium sensor; the current through the specimen, measured as the voltage drop across a 1-Ω resistor; and the potential developed across the specimen gage length, amplified by 10^2 to be of the same magnitude as the other two voltages are scanned by a digital voltmeter. Each of these voltages is read 80 times a minute and the measurements stored on punched paper tape. Data processing is initiated by the first temperature reading above 15 K. The average power and average resistance were computed for each $\frac{1}{4}$-K interval up to 35 K.

True energy release is greater than the measured energy difference between the recovery and comparison runs. The discrepancy is due to heat flow from the irradiated to the unirradiated sections of the specimen. The change ΔW_L in the rate of heat flow from the gage length can be written

$$\Delta W_L = fK(W_D + W_E). \tag{1}$$

The quantity in parentheses is the change from run to run of the difference in energy-generation rates between the irradiated and unirradiated sections, K is the fraction of the irradiated length that lies within the gage length, and f is the fraction of the extra energy that flows out of the gage length. Heat flow is proportional to the temperature gradients in the wire which depend on the thermal history; but since the thermal relaxation time of the specimen is less than three seconds below 28 K and falls with decreasing temperature, whereas the power differences change comparatively slowly, f can be taken as a constant to be determined for the specimen configuration and heating rate. The geometrical factor K was measured from a radiograph of the specimen in the beam.

In Eq. (1) W_D is the rate of energy release due to defect recombination and W_E is the change in Joule heating due to the decrease in defect resistivity during the recovery run. Since at any temperature W_E is nearly proportional to $\Delta\rho$, the defect resistivity removed between that temperature and the end of the recovery run, and, to the extent that $\Delta\rho$ measures the defect concentration, W_D is proportional to $d\Delta\rho/dT$, the two terms can be separated. The Joule heating term is given by

$$KW_E = I^2 \frac{l}{A} \Delta\rho = 1.274 \times 10^{-3} \left(\frac{C_p \Delta\rho}{\rho_T + \Delta\rho} \right), \tag{2}$$

where I is the current through the specimen of cross-section area A, l is the gage length, and ρ_T is the resistivity that does not anneal during the recovery run. In the expression on the right all of the temperature-dependent terms are within the parentheses and for the conditions of the present work the power is given in watts with C_p in J/g K. The data-acquisition program gives I as a function of temperature and $\Delta\rho$ is calculated for each interval so W_E can be computed at any temperature. Values of KW_E at selected temperatures are shown in Table II for recovery after irradia-

TABLE II. Change between recovery and comparison heating runs in excess Joule heating, KW_E.

Temperature (K)	Irradiation 1Q $\Delta\rho$ (10^{-9} Ω cm)	Irradiation 1Q ρ_T (10^{-9} Ω cm)	Irradiation 1Q KW_E (10^{-6} W)	Irradiation 1A $\Delta\rho$ (10^{-9} Ω cm)	Irradiation 1A ρ_T (10^{-9} Ω cm)	Irradiation 1A KW_E (10^{-6} W)
15	5.4	100.6	0.23	3.7	22.7	0.59
20	5.3	136.5	0.34	3.6	58.7	0.515
25	2.0	197	0.13	1.6	120	0.20
30	0.2	291	0.02	0.25	219	0.03

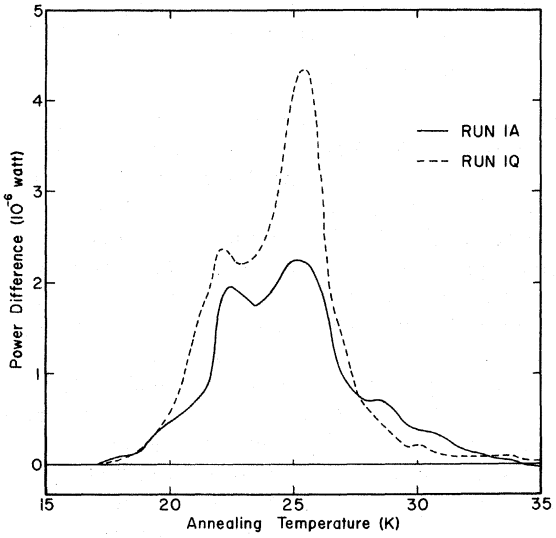

FIG. 4. Energy release as a function of annealing temperature of platinum irradiated as annealed (1*A*) and after quenching (1*Q*).

tions 1*Q* and 1*A*. Below 17 K the difference between recovery and comparison runs is fKW_E. The value of f derived from measurements of this difference and the quantity KW_E computed for each of the six irradiations is 0.38±0.04. Then, if W_M is the corrected measured power difference between runs at any temperature, the rate of energy release within the gage length at that temperature is

$$KW_D = (W_M + fKW_E)/(1-f) \qquad (3)$$

These power differences, computed for each $\frac{1}{4}$ K, are connected by smooth curves and plotted as in Figs. 4 and 5. The total energy release between 17 and 35 K, determined from such plots by measurement with a planimeter, is given in Table I for each of the six irradiations. After the comparison heats of irradiations 1*Q*, 1*A*, and 2*Q*, second comparison heats were performed. The maximum deviation between pairs of comparison runs was less than 0.2×10^{-6} W and the total difference between any pair was less than 10×10^{-6} J.

Stray thermal voltages may introduce serious errors in W_M. To reduce these voltages all leads from the cryostat are maintained in intimate thermal contact along their length and the liquid-nitrogen reservoir, through which these leads pass, was filled at the same time before each run. Tests made during linear heating of the block with no specimen current showed that the thermal voltage generated in the circuit connected to the specimen potential leads changed by less than 3×10^{-7} V during any heat. This maximum change corresponds to an error in measured power of less than 2×10^{-8} W. This is only 5% of the average power due to energy release after irradiation 2*A*, the smallest dose in the present work. The magnitude of the thermal voltage in this circuit is measured at 15 K before each run and the computational program corrects for this voltage.

Changes in thermal voltages in the specimen control circuit are potentially very serious. After several attempts a circuit was produced in which the largest change in thermal voltage detected in

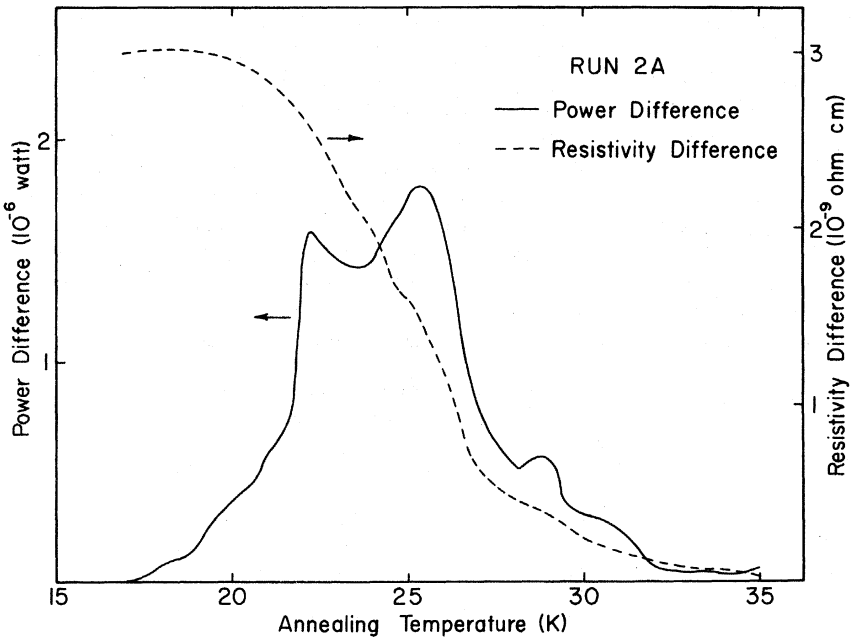

FIG. 5. Simultaneous measurement of energy release and resistivity recovery in stage I after irradiation of annealed platinum.

test heats was 7×10^{-8} V. This maximum shift corresponds to a non-negligible heat flow of nearly 0.2×10^{-6} W. Before each run the compensating voltage in the control circuit is adjusted to neutralize the thermal voltage at 15 K. To compensate for changes in the thermal voltage during each run the mean power difference between recovery and comparison runs from 33 to 35 K, where W_E is negligible, is made proportional to the mean rate of resistivity recovery of that dose in that temperature range. These resistivity recovery rates were determined in subsidiary experiments in which specimens irradiated to a range of doses were heated from 10 to above 35 K while contained in a chamber filled with helium exchange gas. The factor relating resistivity change to energy release was computed from the present data in the interval 25–26 K, where the recovery rate is a maximum. This correction to W_M is varied linearly from zero at 15 K to the value computed as above at 34 K. The maximum correction to the total energy release from this effect was 16×10^{-6} J following irradiation 1*Q*.

Adsorption and desorption of gases from the surfaces of thin specimens can mask the release of energy due to point-defect annealing. Considerable effort was made in this investigation to suppress the effects of gas release during recovery. The specimens were as thick as possible (about one-third the range of the incident particles[23]), consistent with reasonably uniform defect distribution, and had a greater ratio of irradiated volume to surface than in other charged-particle irradiations. The work of Feese indicates that desorption is less significant for platinum than for some other metals.[14] After evacuation of the cryostat the specimen temperature was raised by Joule heating to about 350 K and the specimen remained at this temperature until after the helium reservoir was filled. Except for measurements at 5 K and during linear heating runs, the specimen remained warmer than its surroundings. The measured specific heat without annealing increased smoothly and gave no evidence of gross desorption.

V. DISCUSSION

Throughout most of the interval examined energy release and resistivity recovery measured at the annealing temperature proceed together. This is shown in Fig. 5 for irradiation 2*A*, which had the smallest dose. Resistivity recovery is somewhat distorted compared to the results of standard isochronal anneals with all measurements made at 4.2 K.[17] The distortion results from the temperature dependence of the defect resistivity. This effect is seen clearly at the beginning of the anneal. Below 19 K the decrease in resistivity due to the removal of point defects is overbalanced by the increase in resistivity of the defects which are removed from 19 to 35 K. Owing to the rapid heating rate of this work recovery temperatures are higher than those usually observed[16,17]; the I*D* peak here occurs near 26 K. The temperature shift corresponds to an activation energy for free interstitial diffusion of about 0.06 eV, in agreement with values found in other work.[16,17]

If either the resistivity increment per unit concentration of Frenkel pairs or the energy stored in a pair were known, the other could be calculated from the present data. Unfortunately neither is well known. Theoretical calculations for copper place the interstitial formation energy at three times that of vacancies.[24–26] If this relation applies to platinum the energy of a Frenkel pair in this metal would be 6 eV.[27,28] Combining that value with the observed ratios of energy release to resistivity recovery in the present work yields a resistivity increment of 12×10^{-6} Ω cm for 1-at.% Frenkel pairs. Using the same Frenkel-pair energy a value of 20×10^{-6} Ω cm/at.% was deduced for the Frenkel resistivity from the only other measurements of low-temperature energy release in platinum.[14] The latter work suffered from a large, unexplained background which may have led to an underestimation of the energy released. From an analysis of the dependence of the rate of resistivity increase during irradiation on the direction and energy of primary displacements in platinum, Jung and co-workers obtained $(9.5\pm0.5)\times10^{-6}$ Ω cm/at.%.[29] Considering the uncertainties in the calculations of the energy of a Frenkel pair agreement of their result with the present work is good.

The most extensive data available on energy release in stage I are for copper. From the compilation of Ref. 30 (discarding the two exceptionally low results) the ratio of energy release to resistivity change in copper is 27 ± 4 (J/g)/μΩ cm. Converting the data for both metals to equal numbers of atoms, the ratio of energy release to resistivity recovery in copper is about $3\frac{1}{2}$ times that found here for platinum. Since the calculated Frenkel energy in copper is about 70% that in platinum[24–26] this result implies that the resistivity increment per Frenkel pair in copper is about one-fifth that in platinum. In the work of Ref. 29 the resistivities of Frenkel pairs were determined by identical techniques for both copper and platinum. The ratio of the resistivities was found to be (18±4)%. This comparison should be free of most of the errors attendant upon a calculation of the absolute resistivity in any given metal.

With the fluences used in the present work the resistivity increments produced by irradiations of quenched lattices were greater by (18 ± 3)% than in annealed lattices. As shown in both Fig. 4 and Table I this enhanced resistivity is accompanied by an enhanced release of energy during the anneal. The significant quantity, the ratio of energy release to resistivity recovery, is given in the last column of Table I. This ratio is higher by ($4\frac{1}{2}$ ± $1\frac{1}{2}$)% for the annealed as compared to the quenched specimens and means that the resistivity per defect measured at 5 K due to the defects that recover between 17 and 35 K is increased only a few percent by the presence of a more than order of magnitude greater concentration of vacancies. This slightly larger resistivity per Frenkel pair is sufficient to account for the enhanced initial rate of resistivity increase in quenched platinum during electron irradiation,[6] but for only about one-fourth of the enhanced resistivity in the present work. The calorimetric measurements indicate that during these irradiations about 15% more defects were produced in the quenched than in the annealed specimens.

For primary displacement events to interact sufficiently with quenched-in defects to produce the extra Frenkel pairs these events must sample much more of the lattice than their immediate surroundings. One method is by focused replacement sequences which must have lengths of order 10^2 atomic distances per primary displacement to give the present enhancements.[4,31] This is greater than some theoretical estimates of these lengths,[32] but is in excellent agreement with the length of 186 ± 50 atomic distances per primary displacement found with thermal neutron irradiations of Ni_3Mn.[33] Although the distribution of primary energies resulting from γ emission after thermal neutron capture is much different from the distribution during irradiation with energetic ions the mean primary displacement energy in Ref. 33 was 400 eV as compared to 430 eV in this work. The decrease with increasing dose of the enhanced production occurs on this model from the reduction in the mean length of replacement sequences due to defocusing in the strain fields of interstitials.[34]

To completely establish that interactions at quenched-in defects result in additional Frenkel pairs the energy released during recovery of all radiation-injected defects must be measured. In the present studies somewhat more than half of the resistivity increment at 17 K in the annealed specimens and about 70% of that in the quenched ones are removed by 35K. Above this temperature the recovery rate is very low and calorimetric measurements of the requisite accuracy cannot be made. In addition, at annealing temperatures high enough to remove all defects produced by the irradiation, vacancies from the quench begin to anneal to fixed sites. Simultaneous measurement of the changes in residual resistivity and in lattice parameter during recovery of Frenkel-pair concentrations two orders of magnitude greater than in this work show that the ratio of the resistivity increment to the more fundamental observable remains closely the same throughout the anneal.[9] Since there is no effect of defect concentration on the ratio of resistivity recovery to energy release over the dose range studied here it is unlikely that changes in the specific resistivity of only the few Frenkel pairs to recover after stage I is altered sufficiently by the presence of additional vacancies to give the observed enhancements. The resistivity remaining at the end of recovery after irradiation $2Q$ is less than one-fifth of that present at 17K after irradiation $3Q$.

Additional information can come from a study of the amount that various recovery substages are enhanced by quenching. Substage IC results from the annealing of interstitials deposited close enough to vacancies that their initial change of position is biased toward the vacancy. Production of extra Frenkel pairs at quenched-in defects should deposit more interstitials near to vacancies, Quenching may also increase substage IC statistically by leaving a vacancy close to an interstitial which in an unquenched lattice would not have been a member of a close pair.

Neglecting all clustering, this statistical change, Δf_c, in the fraction of recovery that lies within substage IC is given by

$$\Delta f_c = C_v N_c (1 - f_{cp}) - C_v N_B f_c \ . \qquad (4)$$

In this expression C_v is the concentration of vacancies injected by the quench, N_c is the number of interstitial sites around a vacancy from which IC recovery can take place, N_B is the number of sites closer than IC sites to each vacancy, and f_{cp} and f_c are the fractions of the total number of Frenkel pairs that comprise all close pairs and IC pairs in an irradiated but unquenched lattice. For these irradiations $f_c \sim 16\%$ and $f_{cp} \sim 25\%$; the IC substage is considered to terminate at the minimum near $23\frac{1}{2}$ K in the energy release from unquenched specimens.[16] Taking the vacancy resistivity[35] as 5×10^{-6} Ω cm/at.% gives $C_v \sim 1.5\times10^{-4}$ in the quenched specimens. The sum of N_c and N_B is the stage-I annihilation volume for freely diffusing interstitials; values from 250 to 1700 sites have been fitted to recovery measurements.[36] The athermal recombination volume N_0, which is contained within N_B, is found by combining radiation annealing measurements[37] with the Frenkel-pair

resistivity from the present work to be 150 sites. For all irradiation energies it is observed that

$$1 < \frac{f_c}{f_{cp} - f_c} < 2 , \tag{5}$$

and it is reasonable that a similar relation holds for the sites that the relevant recovery processes originate from, i.e.,

$$1 < \frac{N_c}{N_B - N_0} < 2 . \tag{6}$$

For the quenched-in vacancy concentrations used in the present work the amount of energy released in substage IC was increased on the average by 36%. To produce such an enhancement purely statistically would require, based on Eq. (4), that $N_c + N_B$ comprise 1500 sites for $N_c = N_B - N_0$ and 1050 sites for $N_c = 2(N_B - N_0)$. Between these two extreme cases N_c decreases slowly and monotonically from 670 to 595 sites. It is extremely unlikely that there are 600 sites around each vacancy from which the interstitial has the same bias toward the vacancy while the barrier to recombination from the next closer set of stable sites is smaller by one-third.[16] Such a model is contradicted by the picture of the IC interstitial-vacancy configuration provided by measurements of the change in elastic moduli.[38]

The large annihilation volumes ($N_B + N_c$) required to produce, without invoking enhanced displacements at quenched-in defects, the observed increases in substage IC are within the upper limits allowed by the analysis of Sonnenberg and coworkers,[36] but are ruled out by other measurements. The data of Ref. 16 upon which their analysis is based show (using the Frenkel resistivity from the present work) that Frenkel-pair concentrations up to 2×10^{-4} do not change the fraction of total recovery that occurs in close-pair substages. Using the minimum necessary value of $N_B + N_c$ and inserting f_{cp} appropriate to the irradiations of Ref. 16, the fraction of recovery in substage IC and below should be more than 8% greater for the largest dose than for the smallest. Indeed, if the enhanced resistivity changes during irradiation and low-temperature annealing of quenched platinum are to be explained entirely by deviations from Matthiessen's rule,[37] then for the larger doses of Ref. 16 very large changes in fractional close-pair recovery must occur. In addition, low-dose near-threshold electron irradiations, for which long replacement collision sequences are not expected to be important,[39] show that with $C_v \sim 0.5 \times 10^{-4}$ no measurable change occurred in the fraction of recovery attributable to close-pair processes,[40] whereas nearly 2% increase should be seen if the close-pair recombination volume were 1000 sites. In all of the heavily doped or quenched specimens of Refs. 16 and 41, greatly enhanced recombination rates are seen when mobile interstitials begin to sample a significant portion of the lattice.

VI. CONCLUSIONS

(i) Changes in electrical resistivity measured at temperatures close to the boiling point of liquid helium are, to within a few percent, proportional to changes in the Frenkel-pair concentration, even in the presence of much greater concentrations of vacancies injected by a prior quench.

(ii) The resistivity increment due to defects in irradiated platinum which anneal in the latter part of stage I is appreciably greater when measured at the recovery temperature than when measured at 5 K.

(iii) The larger part of the enhanced resistivity increments in quenched platinum found during low-temperature low-dose irradiations with ions or neutrons result from the production of additional Frenkel pairs. The considerably smaller enhancements found during near-threshold electron irradiations may be due mainly to deviations from Matthiessen's rule.

(iv) The extra defects produced in quenched platinum are deposited preferentially in sites close to vacancies.

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