

breakdown point. The central crown orbit is observed in the (0001) plane and (11 $\bar{2}$ 0) plane data for field orientations where breakdown is occurring, with only the decrease in amplitude of the first few harmonics as mentioned above.

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## Recovery of Deuteron-Irradiated Platinum\*

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Pure, well-annealed platinum specimens and platinum specimens containing quenched-in vacancies were bombarded near 5°K with 20-MeV deuterons. Both damage production and recovery were studied. The quenched-in vacancies increase both the initial production rate and the fall in this rate with increasing deuteron dose. A model based upon defocusing at divacancies is used to explain these features. Recovery of the damage occurred in four main stages. The excess vacancies affect the amount of recovery and/or the temperature of maximum recovery rate in each stage. Recovery also depends on the dose. The principal annealing processes in each stage are identified as: stage I, close-pair recombination and free migration of interstitials; stage II, release of mobile interstitials from traps; stage III, migration of a second type of interstitials; stage IV, vacancy migration.

#### INTRODUCTION

**A**FTER many years of research there still is not general agreement as to the properties of defects produced by irradiation of pure metals at low temperature. Many of the features of defect production and recovery in pure metals can be explained by more than one model. Additional constraints that reduce the number of possible models are imposed if the pure metal is doped before irradiation with entities that interact with radiation-produced defects. Ideally these entities should have the following properties:

1. It should be possible to predict their reactions with the various types of defects injected by irradiation.
2. It should be possible to inject them uniformly through the lattice and in a wide range of concentrations.
3. They should measurably perturb radiation defect production and/or recovery.
4. They should not be accompanied by appreciable numbers of other entities with unknown interactions.

Many doped metal irradiations have been reported.<sup>1-4</sup> Most frequently the pure metal has been doped by

introducing substitutional impurities or by plastic deformation. Both of these dopings are far from ideal. The interactions between foreign atoms and radiation-produced interstitials and vacancies are not well known, and the impurities may precipitate. The dislocations produced by plastic deformation are far from uniformly distributed, and point defect-dislocation reactions are also not completely understood.

It is often more informative to dope with lattice vacancies. Their interaction with interstitials is simple annihilation. By quenching, vacancy concentrations greater than 10<sup>-4</sup> can be injected without introducing other defects. In a few metals enough quantitative knowledge has been gained so that the vacancy concentration and distribution resulting from a quench can be reasonably well calculated and the kinetics of vacancy migration and the sinks for supersaturated vacancies known.

Platinum is probably the best metal for such quenching, followed by irradiation experiments. The as-quenched state in platinum is stable at room temperature so specimens can easily be prepared and mounted for irradiation. Vacancy clustering is not important in platinum,<sup>5</sup> so the analysis is particularly simple. Platinum specimens of high purity can be readily prepared,

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<sup>1</sup> C. L. Snead and P. E. Shearin, *Phys. Rev.* **140**, A1781 (1965).

<sup>2</sup> K. Herschbach and J. J. Jackson, *Phys. Rev.* **138**, 661 (1967).

<sup>3</sup> C. J. Meehan, A. Sosin, and J. A. Brinkman, *Phys. Rev.* **020**, 411 (1960).

<sup>4</sup> M. L. Swanson and G. R. Piercy, *Can. J. Phys.* **42**, 1605 (1964).

<sup>5</sup> J. J. Jackson, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic Press Inc., New York, 1965) p. 467.

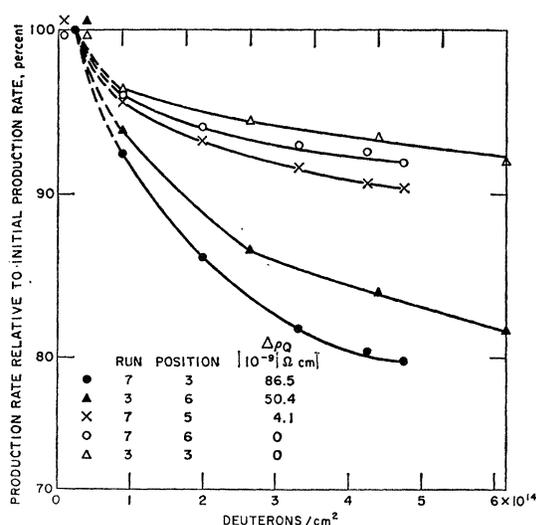


FIG. 1. Radiation annealing in platinum, the incremental damage rate ( $\Delta R/\Delta$  dose) is given as a fraction of the damage rate in the first increment. The influence of quenched-in vacancies on radiation annealing is shown.

and the purity is maintained after quenching and reannealing.<sup>6</sup>

This paper gives the results of detailed comparisons between various platinum specimens with respect to production of defects by irradiation below 10°K with 20 MeV deuterons and with respect to the recovery of these defects. Some of the specimens were well annealed before irradiation and others were quenched so as to give several different vacancy supersaturations. Based on these results we proposed a model for defect production and radiation annealing in platinum and we are able to give a more complete identification of the processes responsible for thermal annealing of the defect structure after irradiation.

### EXPERIMENTAL

The specimens were prepared from wire chemically purified to 99.999% purity and supplied hard drawn to 0.002 inch diameter by the Sigmund Cohn Company. This wire was then further refined thermally in our laboratory.<sup>6</sup> The ratio of resistance at 273°K to that at 4.2°K for these specimens was greater than 2500. The data of Huebener<sup>7</sup> indicate that about half of this resistivity at 4.2°K is due to scattering of electrons from the surface of the 0.002 in. wire. The remaining resistivity corresponds to an impurity concentration of probably less than 1 ppm.

The quenched specimens were prepared from 0.002 in. wire that had been annealed as above. The specimens were heated to the quench temperature by the passage of electric current while contained in a draft-free box under three atmospheres pressure of air. The

average specimen temperature was calculated from its electrical resistance. The temperature variation over the specimen length as determined by an optical pyrometer was less than 10°C, which means that near the melting point the vacancy concentration was uniform to within 2%. The wires were quenched by suddenly reducing the heating current to 3% of the value needed to maintain the quench temperature. The cooling rate was measured by displaying the voltage across the specimen on an oscilloscope. Below 1000°C the cooling curve is nearly exponential since almost all of the heat loss is by convection and conduction. Above 1000°C radiative heat loss was large enough to be measurable. The time to cool from 1600°C to 800°C was  $25\text{--}30 \times 10^{-3}$  sec.

The irradiations were carried out at the Argonne National Laboratory 60-in. cyclotron. The cryostat and auxiliary equipment have been described previously.<sup>8</sup> This cryostat allows us to irradiate as many as six specimens simultaneously and give them identical thermal treatments during annealing; but in some of the irradiations, specimens other than quenched or annealed platinum were mounted in some of the positions. Two of the specimens can be shielded by a movable shutter and given a dose different from what the other four receive.

In our first irradiations<sup>9</sup> dummy annealed specimens were also mounted in the deuteron beam; the temperatures of these dummies were monitored with thermocouples, and the deuteron flux was adjusted so that the measured dummy temperatures remained below 8°K. This procedure was not good enough to keep the temperature of the most heavily damaged specimens below 8°K during irradiation. Such specimens showed very little recovery below 10°K. In later irradiations the deuteron current was kept below  $20 \times 10^{10}$  deuterons/cm<sup>2</sup> sec. Recovery data show that all specimens bombarded with this current remained below 7°K.

Only the total deuteron current through the specimen chamber is measured so the exact deuteron flux at each point is not known. Before each irradiation the beam is adjusted so that a radiograph shows it to be spread evenly over the region occupied by the specimens but it does not necessarily remain homogeneous during the bombardment. Because of the arrangement of our specimens, those specimens in positions  $n$  and  $n+3$  for  $n=1, 2, \text{ or } 3$  receive nearly identical deuteron fluxes which, however, may be different from the fluxes at the other specimens.

The damage was measured by the change in resistivity of the specimens. The reproducibility of the electrical measurements on any one specimen was better than  $2 \times 10^{-12}$  ohm cm; however, the exact length of a specimen that was irradiated is uncertain to about 10%. Comparisons of absolute resistivity changes

<sup>6</sup> J. J. Jackson, *Problems in Ultra-Pure Materials*, edited by E. Rexer (Akademie-Verlag, Berlin, 1966) Vol. 1.

<sup>7</sup> R. P. Huebener, *Phys. Rev.* **140**, A1836 (1965).

<sup>8</sup> K. Herschbach, *Rev. Sci. Instr.* **37**, 171 (1966).

<sup>9</sup> K. Herschbach and J. J. Jackson, *Phys. Rev.* **153**, 689 (1967).

between different specimens are uncertain by about that amount. The resistivity increments from the various irradiations varied over a range of two orders of magnitude from  $1.4 \times 10^{-9}$  to  $140 \times 10^{-9}$  ohm cm.

The annealing procedure was quite similar to that described in our earlier papers;<sup>2,10</sup> i.e., the specimens were pulsed to a monotonically increasing series of annealing temperatures held at temperature for several minutes, then cooled to below 5°K for resistance measurements. A difference between this work and that reported earlier is that in the present case the time held at annealing temperature was not a constant but rather was six min. when the temperature increment was less than 2% of the previous annealing temperature, eight min. for increments between 2 and 4%, and ten min. for increments greater than 4% of the previous temperature. Measurements of the specimen resistances showed that all specimens used in this report remained in excellent thermal contact with the specimen holder. All came to equilibrium at the annealing temperature less than 0.5 sec after the holder reached temperature; all begin to cool as soon as the heating current was turned off.

## RESULTS

### A. Damage Production

In a previous paper<sup>9</sup> we reported measurements of the dependence on dose of the defect production rate in fcc metals irradiated below 10°K. On the basis of these measurements we set forth two general propositions:

1. The initial defect production rate is greater in doped than in pure, annealed lattices.

TABLE I. Initial defect production rates.

Run	Position	Quenched-in resistivity ( $10^{-9}$ ohm cm)	Resistivity increase first 100 $\mu$ C <sup>a</sup> ( $10^{-9}$ ohm cm)
3	3	0	3.3
	6	50.4	3.8
6	1	86.5	3.9
	4	0	3.3
7	1	86.5	3.85
	3	86.5	4.0
	4	0	3.2
	5	4.1	3.3
9	6	0	3.2
	1	0	3.2
10	4	77.5	3.55
	2	38	3.25
13	3	11	3.0
	5	18	3.2
	6	0	2.8
	2	28	3.5
13	4	0	2.95
	5	0	2.85
	6	3.5	2.8

<sup>a</sup> 100 $\mu$ C collected charge =  $4.4 \times 10^{14}$  deuterons/cm<sup>2</sup>.

<sup>10</sup> K. Herschbach and J. J. Jackson, Phys. Rev. 153, 699 (1967).

TABLE II. The Effect of dose on stage I recovery.

Run	Quenched-in resistivity ohm cm $\times 10^{-9}$	Increase in resistivity from irradiation ohm cm $\times 10^{-9}$	Damage remaining at 35°K percent
7	0	3.8	37.99
	0	31.2	39.31
8	0	3.5	37.46
	0	25.2	39.15
9	0	1.6	37.48
	0	14.15	38.25
7	86.5	4.5	24.61
	86.5	35.5	28.46
11	64.5	4.75	25.25
	64.5	35.0	28.54
2	0	133.8	43.63
	51	137.7	37.86

2. Radiation annealing (the decrease in production rate with increasing dose) is greater in doped than in undoped lattices. In a second paper<sup>10</sup> we showed that both of these results can be explained on the basis of interactions of long range transport events with lattice defects. Further measurements, some of which are shown in Fig. 1 and Table I, support the conclusion of these earlier papers.

Our measurements of relative changes in defect production rates between a pair of specimens mounted at positions  $n$  and  $n+3$  in a given run are quite accurate. These data show that the amount of radiation annealing increases with increasing quenched-in vacancy concentration. As described above, considerable uncertainty is involved in our measurements of absolute defect production rates. Within the limits of this uncertainty there is no enhancement of the initial production rates over annealed specimens in those specimens quenched from lowest temperatures (Run 7 No. 5 and Run 13 No. 6); but there is significant enhancement of the initial production rate with larger concentrations of quenched-in vacancies.

### B. Recovery in Stage I

The recovery between 10 and 40°K of well-annealed platinum irradiated with 20 MeV deuterons to give a resistivity increase of  $31 \times 10^{-9}$  ohm cm is shown as the solid line in Fig. 2. Selected data for two annealed specimens irradiated to give much different defect concentrations and for a quenched specimen are also shown. The slopes of the recovery curves for four of the specimens from Run No. 7 (all subjected to identical annealing temperatures) are plotted in Fig. 3. Only four annealing peaks can be resolved. There is a tail on the high temperature side of the largest peak but we have not resolved structure in it even with temperature increments as small as 0.25°K. The number of recovery peaks found in this work is far fewer than the number found

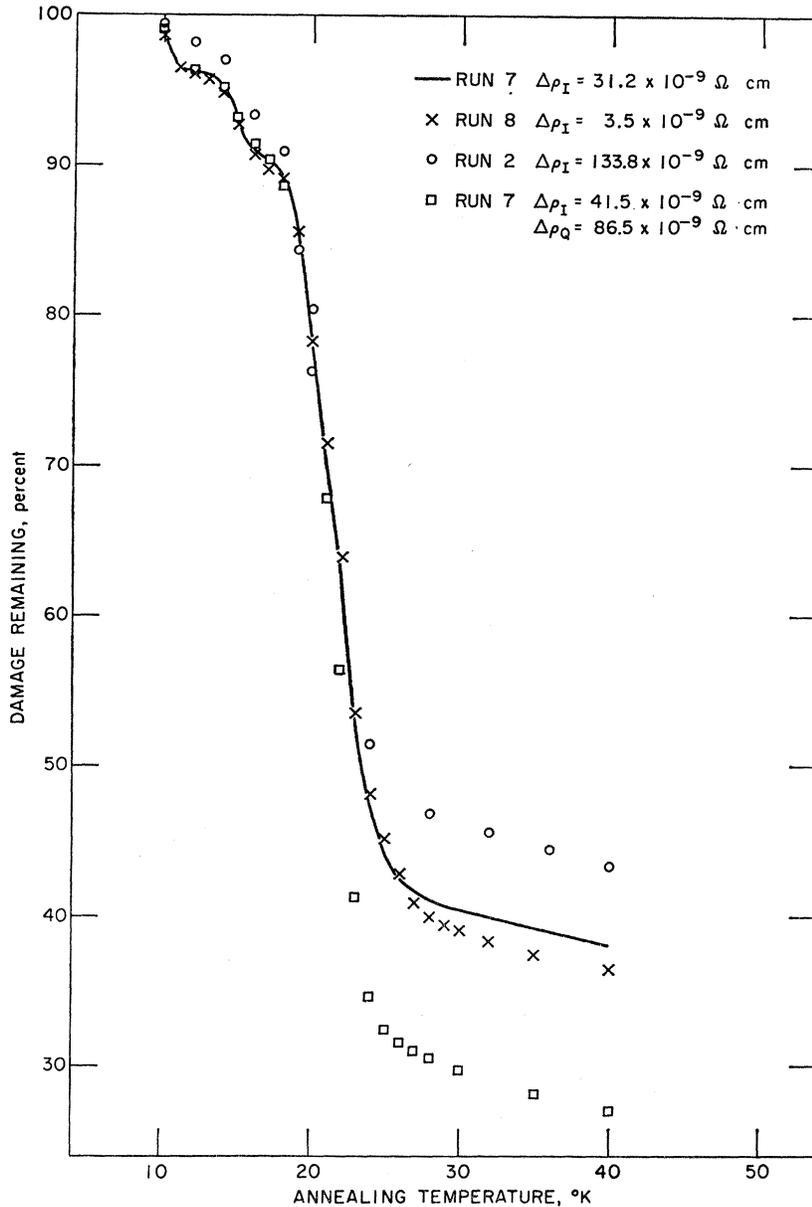


FIG. 2. Stage I in deuterium irradiated platinum.

in Stage I recovery in copper<sup>11</sup> and aluminum;<sup>12</sup> but does agree with the findings of Bauer and Goepfinger<sup>13</sup> for recovery of electron-irradiated platinum and with those of Coltman *et al.*<sup>14</sup> and Burger *et al.*<sup>15</sup> after neutron irradiation. The relative sizes of the recovery peaks does depend upon the type of irradiation. This will be discussed below.

<sup>11</sup> G. W. Iseler, H. I. Dawson, A. S. Mehner, and J. W. Kauffman, *Phys. Letters* 17, 212 (1965).

<sup>12</sup> H. I. Dawson, G. W. Iseler, A. S. Mehner, and J. W. Kauffman, *Phys. Letters* 18, 247 (1965).

<sup>13</sup> W. Bauer and W. F. Goepfinger, *Phys. Rev.* 154, 588 (1967).

<sup>14</sup> R. R. Coltman, C. E. Klabunde, K. L. McDonald, and J. K. Redman, *J. Appl. Phys.* 33, 3509 (1962).

<sup>15</sup> G. Burger, K. Isebeck, J. Volkl, and H. Wenzl, *J. Appl. Phys.* 36, 3356 (1965).

### 1. Dose Dependence

The effect on recovery of changes in one parameter can best be seen if all other parameters that can affect recovery are held constant. This ideal has been closely approached in some of our measurements of the effect of dose. Several pairs of specimens were prepared, annealed or quenched, as one wire and then cut apart and mounted for irradiation. They were irradiated in the same run, with low dose specimen shielded by a shutter during part of the irradiation, and then annealed together. The only source of differences between members of the pair before irradiation should be mounting strains; and if a specimen was visibly strained we discarded both members of the pair. Data on several such

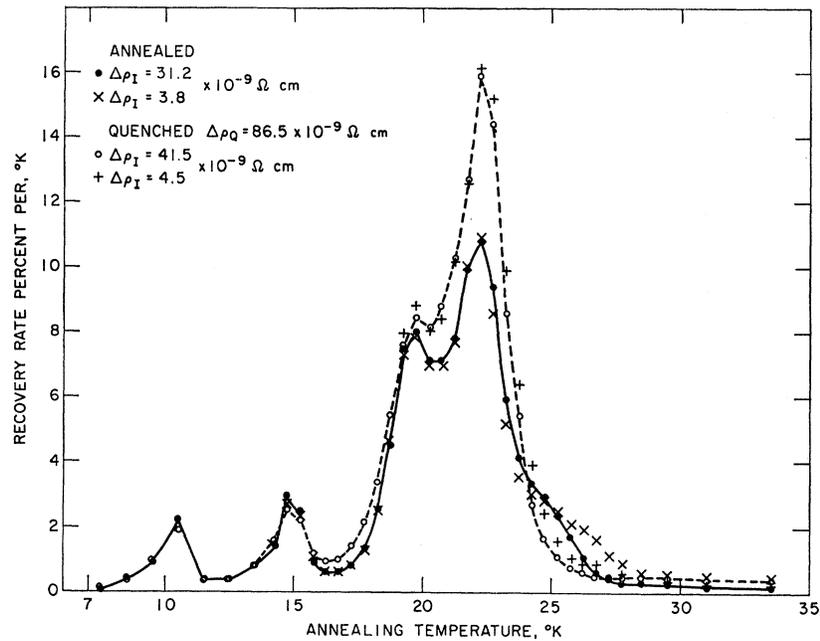


FIG. 3. Derivative of the isochronal annealing curve (stage I) of Pt from run No. 7.

pairs are given in Table II. Two other specimens irradiated to much higher doses are also included in this table.

Recovery of three pairs (the others were similar) is shown in Fig. 4. To emphasize the differences in recovery due to differences in dose this figure is constructed using the technique we described in detail in Ref. 2. The percentage of damage remaining in each member of the pair is calculated after each annealing step and the percentage remaining in the smaller dose member is subtracted from that remaining in the larger dose member. Below 22°K dose has very little effect on recovery. Between 22 and 27°K there is nearly 4% more recovery in the small than in the large dose quenched specimen. Above 27°K the annealing rates are again nearly independent of dose. In nonquenched specimens, beginning at a slightly higher temperature the low-dose specimens anneal first slower then faster than the high-dose specimens. Above 35°K the recovery rate in the low-dose specimens falls behind again. The maximum changes in percent recovery due to dose in Stage I are little more than 1% of total damage for nonquenched specimens.

## 2. Energy of the Recovery Processes

The resistivity of one specimen was continuously measured during each annealing pulse in run No. 5. The annealing pulses were twenty minutes long and increased in increments of 1.5°K. This specimen had been annealed before irradiation and was irradiated to a resistivity increment of  $31.5 \times 10^{-9}$  ohm cm. These combined isothermal and isochronal annealing data were analyzed by the method of Primak<sup>16</sup> as modified

<sup>16</sup> W. Primak, J. Appl. Phys. **31**, 1524 (1960).

by Herschbach<sup>17</sup> to give the activation energy spectrum shown in Fig. 5. The isothermal measurements could not be continued above 25°K because resistivity changes from small thermal fluctuations masked the relatively small resistivity changes from recovery that occur above that temperature.

This method of constructing an activation energy spectrum can lead to serious errors if resistivity changes measured at the various annealing temperatures do not correspond to decreases in the defect concentration. Such behavior has been observed for aluminum<sup>17</sup> and

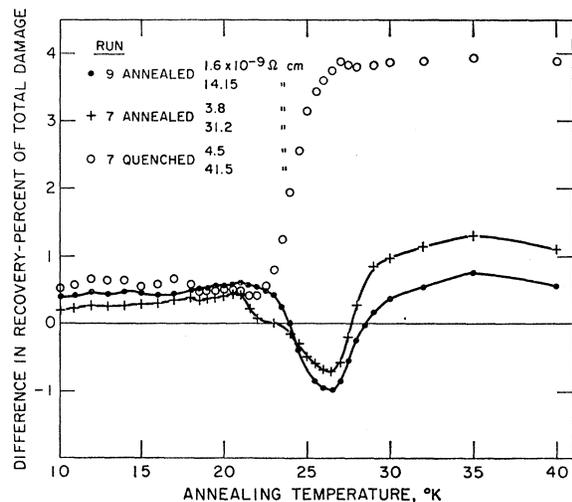


FIG. 4. The difference in recovery (the percentage of damage remaining in a high-dose specimen minus the percentage remaining in a low-dose specimen) versus the annealing temperature.

<sup>17</sup> K. Herschbach, Phys. Rev. **130**, 554 (1963).

TABLE III. Comparison of resistance decreases measured at annealing temperature with decreases measured at 4.2°K.

Annealing temperature (°K)	Resistance decrease ( $\mu\Omega$ )	
	At annealing temperature	at 4.2°K
13	26	27.8
14.5	78	70.6
16	127	139.5
17.5	59	63.6
19	234	210.5
20.5	512	503.2
22	546	557.8
23.5	585	601.8
25	246	260.4
Total	2415	2435.2

gold.<sup>18</sup> In both of these metals there are annealing stages in which the decreases in resistivity measured at some annealing temperatures are greater than the corresponding decreases measured at 4.2°K. Table III gives the relevant data for our platinum specimen. There are differences as great as 10% between entries in the two columns but the randomness of the differences makes it appear as though the differences are due to errors in measuring the resistance change at annealing temperature. In addition, the sum of the resistance changes at 4.2°K is greater than the sum at the annealing temperatures, contrary to what would be observed if the resistivity changes from deviations from Matthiessen's Rule were a significant fraction of the resistivity increment from the defects that anneal in this temperature range. The Primak-Herschbach analysis should be free from errors from such deviations in the present case.

### 3. Effect of Type of Irradiation

Recovery after irradiation with electrons<sup>13</sup> or neutrons<sup>14,15</sup> resembles recovery after deuteron irradiation in that distinct annealing peaks are seen near 10°K

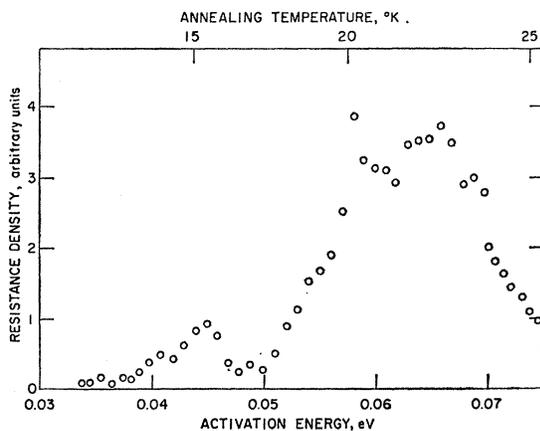


FIG. 5. The activation energy spectrum from the Primak-Herschbach analysis.

<sup>18</sup> K. Herschbach and J. J. Jackson, *Bull. Am. Phys. Soc.* **10**, 1099 (1965).

and near 15°K and in that the greatest amount of annealing in Stage I takes place between 19 and 24°K. However, the fraction of the added resistivity that recovers in Stage I decreases as the average energy of a primary displacement increases. This is shown in Table IV.

The relative heights of the four prominent annealing peaks and their resolution also vary with the type of irradiation. With electrons all peaks are at least twice as high as the valleys between. The peak near 20°K is the largest and the two low temperature peaks are from  $\frac{1}{2}$  to  $\frac{3}{4}$  the height of that near 22.5°K. With neutrons the two high-temperature peaks are not resolved and the two low-temperature peaks are only 10 to 15% of the height of the large peak. Our results with deuterons lie between these extremes.

### 4. The Effect of Quenched-in Vacancies

The presence of vacancy concentrations of the order of  $(2 \pm 1) \times 10^{-4}$  before irradiation leads to large changes in the magnitude of the subsequent recovery. This can best be seen by comparing the recovery of quenched and of annealed specimens that have received nearly equal deuteron fluxes and identical annealing treatments.

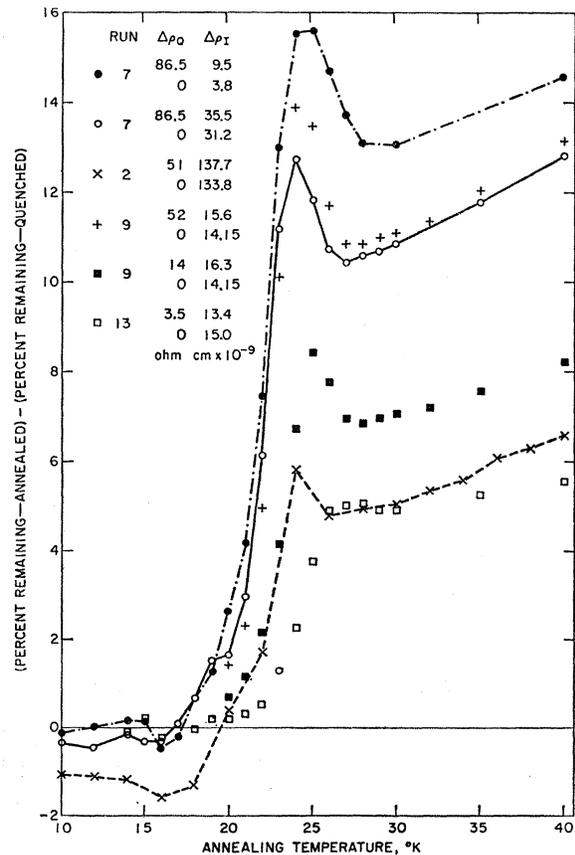


FIG. 6. The difference in recovery (the percentage of damage remaining in a nonquenched specimen minus the percentage remaining in quenched specimen) versus the annealing temperature.

TABLE IV. Low-temperature recovery in platinum after various irradiations.

Irradiating particles	1 MeV <sup>13</sup> electrons	20 MeV deuterons		Thermal <sup>a</sup> neutrons	Fast <sup>a</sup> neutrons	Munich reactor <sup>b</sup> neutron spectrum
Dose (10 <sup>-9</sup> Ω cm)	1.7	3.5	133.8	6.2	5.9	4.6
Damage remaining after anneal at 30°K (Percent of total)	10	39	46.3	42.5	60	68

<sup>a</sup> See Ref. 14.<sup>b</sup> See Ref. 15.

This comparison is shown in Fig. 6 for six such pairs. Below 18°K the quenched-in vacancies affect the fractional recovery by less than  $\frac{1}{2}\%$ . The wiggles in the curves between 10 and 18°K result mainly from the broadening of the annealing peaks in quenched platinum with respect to those in platinum that has not been quenched.

Above 18°K fractional recovery is enhanced by quenching. The greatest absolute increase in recovery rate coincides with the temperature interval of maximum recovery. The enhancement of fractional recovery reaches a maximum near 24°K, falls again during the interval when the recovery rates are decreasing, and then gradually rises in the region of low recovery rate above 30°K. The amount of enhancement (difference in percent recovered) increases as the ratio  $(\Delta\rho_Q/\Delta\rho_I)^{19}$  of the quenched specimen increases and for equal ratios increases strongly with  $\Delta\rho_Q$ . There is very little enhancement below the temperature of maximum annealing rate in the quenched specimen with the smallest concentration of vacancies (Run 13).

Despite the large changes in the magnitude of some of the Stage I annealing peaks, the temperature of maximum recovery is not shifted by a measurable amount in any of these peaks (Fig. 3).

### C. Recovery between Stage I and 300°K

The complete isochronal recovery curves for high dose quenched and nonquenched platinum specimens are shown in Fig. 7. The negative values for the high temperature end of the quenched curve represent the removal of the quenched-in vacancies in addition to removal of the defects added by irradiation. After Stage I the annealing rate is low until a small recovery stage centered near 320°K is reached. After this stage there is little recovery until the remaining resistivity is removed in a stage centered near 570°K.

It is impractical to anneal at temperatures above 300°K in the cryostat so the specimens must be removed and remounted to continue recovery to higher temperature. For this reason recovery below 300°K is discussed separately from recovery above 300°K.

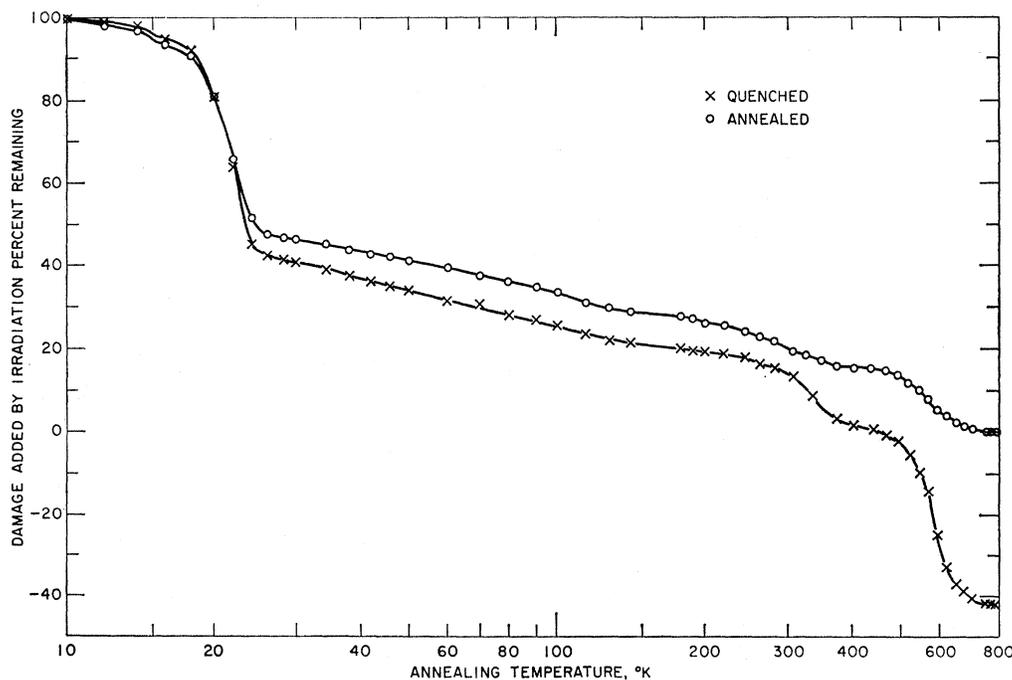


FIG. 7. Complete recovery curves for Pt irradiated with 20 MeV deuterons. The apparent negative annealing represents recovery of the quenched-in defects.

<sup>19</sup>  $\Delta\rho_Q$  is the resistivity added by the quench.  $\Delta\rho_I$  is the resistivity added by the irradiation.

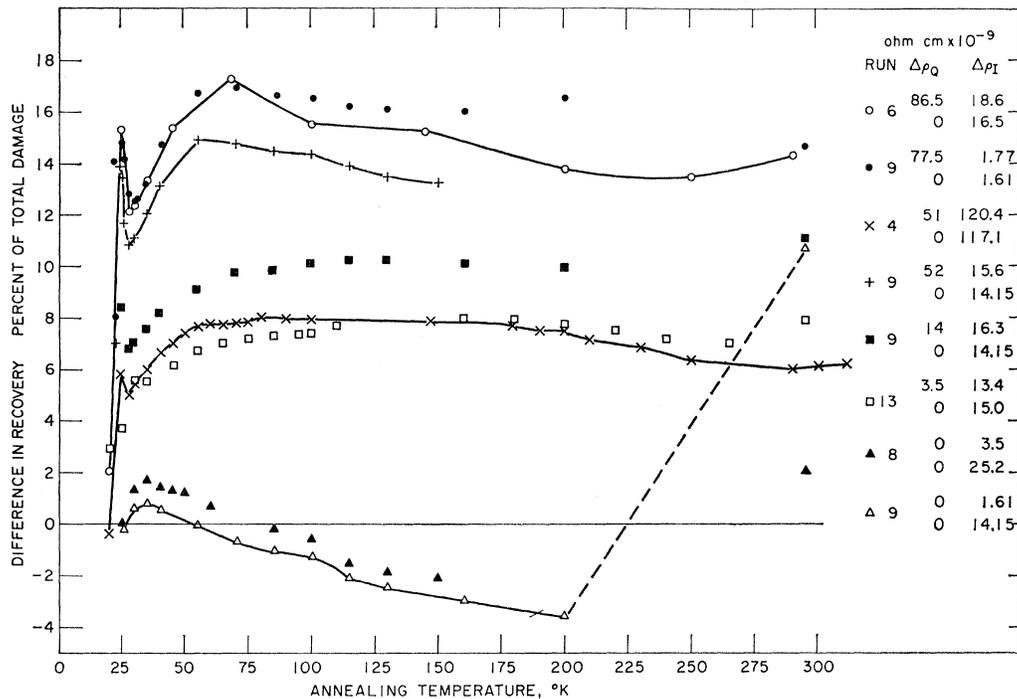


FIG. 8. The difference in recovery (the percentage of damage remaining in a nonquenched and/or high-dose specimen minus the percentage remaining in a quenched and/or low-dose specimen) versus the annealing temperature.

Only about  $\frac{1}{8}$  of the resistivity added by deuteron irradiation anneals between 35 and 240°K. This corresponds to what is called stage II recovery in other FCC metals. In platinum there is only one clearly resolved substage, that near 110°K, in this interval.

Recovery depends strongly on dose in stage II. This dependence is shown in Fig. 8 for two pairs of unquenched specimens; the members of each pair were given identical treatments except for doses differing by a factor of  $8 \pm 0.8$ . The specimens with larger doses recover faster than those with smaller doses up to at least 200°K. Percentage recovery in the smaller is only  $\frac{2}{3}$  of that in the larger between 35 and 200°K and is relatively the smallest at the upper end of this range. Between 200 and 300°K there is a reversal, and fractional recovery becomes much greater in specimens given small doses.

The annealing rate is greater in all quenched specimens than in the corresponding nonquenched specimens from 28°K to perhaps 60°K. Above that temperature, beginning with specimens of the largest ratio

( $\Delta\rho_Q/\Delta\rho_I$ ) the quenched specimens successively begin to recover less rapidly than nonquenched ones until near 200°K all quenched specimens are annealing slower than their corresponding nonquenched partners. Near 300°K, stage III recovery, quenched specimens once again anneal faster than specimens that were not quenched. Detailed comparisons of several pairs of quenched and nonquenched specimens are shown in Fig. 8. Particularly to be noted is that all quenched specimens have their greatest absolute lead in recovery over their nonquenched partners in stage II.

#### D. Recovery Above 300°K

Only the two pairs of specimens that received the largest doses, quenched and not quenched specimens from runs 2 and 4, were remounted for measurements above 300°K. The resistivity remaining at this temperature in other specimens was so low that remaining recovery would be badly distorted by the small resistivity changes resulting from inadvertent strains while remounting the specimens. Table V shows the effect of remounting on the resistivity of the four specimens measured above 300°K.

The data in Table V show that the strains incurred in removing the specimens from the cryostat and clamping them to another specimen holder increased the resistivity of the annealed specimens and reduced the resistivity of the quenched ones. Qualitatively, these changes are in the direction expected from previous work on room temperature deformation of

TABLE V. Changes in extra resistivity upon remounting.

Specimen	Resistivity remaining after 311°K anneal in cryostat ( $\Omega\text{-cm} \times 10^{-9}$ )	Resistivity removed above 311°K ( $\Omega\text{-cm} \times 10^{-9}$ )
2A	27.4	28.8
4A	24.1	25.5
2Q	69.6	64.2
4Q	66.8	62.1

TABLE VI. Resistivity recovered in stage I<sup>a</sup>

Nominal dose (10 <sup>14</sup> d/cm <sup>2</sup> )	$\Delta\rho_Q$ $\Omega\text{-cm}\times 10^{-9}$	$\Delta\rho_I$ $\Omega\text{-cm}\times 10^{-9}$	Resistivity recovered between $\Omega\text{-cm}\times 10^{-9}$			
			14-16°K	19-21°K	21-23°K	23-28°K
2.2	0	1.61	0.06	0.24	0.31	0.21 <sup>b</sup>
	77.5	1.77	0.06	0.29	0.48	0.25 <sup>b</sup>
5.12	0	3.8	0.15	0.55	0.8	0.55
	86.5	4.5	0.16	0.75	1.3	0.6
22.0	0	15.1	0.6	2.2	2.8	2.0
	3.5	14.4	0.55	2.0	2.7	2.0
	14	15.3	0.65	2.25	3.15	2.05
	28	14.8	0.55	2.3	3.4	2.05
	52	15.6	0.6	2.55	3.7	2.0
	86.5	18.6	0.65	3.05	5.1	1.95
49.1	0	31.2	1.2	4.65	5.75	3.5
	86.5	35.5	1.25	5.4	8.8	3.6
211.2	0	133.8	4.85	17.1	22.4	13.2
	51	137.7	4.7	19.15	26.5	13.6

<sup>a</sup> Where several specimens have received the same treatment the average for the group is presented in this table.

<sup>b</sup> Resistivity recovered between 23-29°K is shown for these specimens.

quenched and annealed platinum;<sup>20</sup> but without an independent measure of the strains involved here, a quantitative comparison is impossible. The present data indicate that these specimens received the equivalent of about 1% tensile strain. It is particularly unfortunate that the temperature at which the specimens must be remounted is in an interval in which recovery has been seen in electron irradiated<sup>21</sup> and in cold-worked platinum.<sup>22</sup>

This recovery stage is also seen after deuteron irradiation (Fig. 7). Recovery is much larger in quenched specimens than in specimens not quenched before irradiation despite the resistivity losses suffered by the former in remounting. The final recovery stage seen in all deuteron irradiated specimens is also seen in electron irradiated<sup>21</sup> and in deformed platinum.<sup>22</sup> All of the excess resistivity introduced into platinum by quenching alone also recovers in this temperature region.<sup>5</sup>

## DISCUSSION

### A. Production and Recovery of Close Frenkel Pairs

The most prominent features in the low-temperature recovery of deuteron-irradiated platinum are the four recovery peaks centered near 10, 15, 20, and 22.5°K. Figure 3 shows that the temperature of maximum recovery rate in all of these peaks is not shifted by changes in dose or by the presence of quenched-in vacancies. If a recovery stage is due to the migration of a defect that samples a representative portion of the lattice on its way to a sink then the temperature of this stage will decrease with increasing sink concentration, since as the sink density increases the typical defect needs fewer thermally activated jumps to be annihilated. The sink density for the more mobile

defect of the Frenkel pairs produced by radiation increases with increasing dose; and if the interstitial is more mobile than the vacancy, quenched-in vacancies also increase the sink density for interstitials. Approximate expressions for the temperature decreases to be expected from larger doses and from quenched-in vacancies for a peak due to long range migration of interstitials have been given by Bauer and Sosin.<sup>23</sup> These expressions predict that for the specimens whose recovery is shown in Fig. 3 the peak at 22.5°K should be shifted downward, relative to the low-dose unquenched specimen, 1.6°K in the high-dose unquenched specimen and 2.6°K in the low-dose quenched specimen, taking  $E$ , the activation energy of the recovery process, as 0.065 eV. Since  $E$  is approximately proportional to the annealing temperature, the temperature of maximum recovery rate in any of the three lower peaks that is due to long range migration of an interstitial

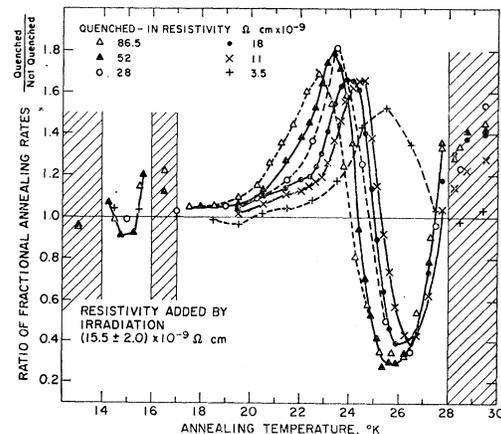


Fig. 9. The ratio of the normalized recovery rates  $[(\Delta R/\Delta T)/\Delta\rho_I]$  of several pairs of quenched versus not quenched specimens. The shaded areas are regions of small annealing rate.

<sup>20</sup> J. J. Jackson, Bull. Am. Phys. Soc. **10**, 337 (1965).

<sup>21</sup> W. Bauer and A. Sosin, Phys. Rev. **147**, 482 (1966) second series.

<sup>22</sup> See Ref. 55, p. 479.

<sup>23</sup> W. Bauer and A. Sosin, Phys. Rev. **136A**, 255 (1964).

should be decreased by from 4/9 to 8/9 of the above shifts. Since no such temperature shifts are seen in the annealing up to near 23°K, none of this annealing can be due to long range migration of a defect.

Although quenched-in vacancies do not change the peak temperatures of the recovery substages occurring below 23°K, these excess vacancies do, in general, increase the amount of recovery both in the substage at 15°K and particularly in the large substages in the interval 19–23°K. This is emphasized in Fig. 9 in which are plotted the ratios of the recovery rates of several quenched specimens to the rates of nonquenched specimens irradiated and annealed simultaneously, as suggested by Sosin.<sup>24</sup> This method of combining and presenting the data retains the advantages gained by giving the specimens whose ratios are plotted identical annealing treatments. The ratios plotted here are normalized by dividing the resistance decrease in each temperature interval by the total resistance added by irradiation so that a ratio of unity means the same fractional recovery in both specimens regardless of total dose. The enhancement of fractional recovery (ratio) in the interval 19–23°K is very small for the smallest concentration of quenched-in vacancies and increases with increasing vacancy concentration. The resistivity decreases observed in specimens given a variety of different treatments are listed in Table VI. Again we must emphasize that while errors of 10% can be involved in comparing absolute resistivity changes in one specimen with changes in another specimen the errors in the relative changes ( $\Delta\rho/\Delta\rho_I$ ) for any one specimen are at least an order of magnitude smaller for all entries in Table VI.

These data show that when large vacancy concentrations are quenched-in, the number of close pairs responsible for the annealing peak at 15°K changes in about the same proportion as does the total defect concentration and that the number of close pairs responsible for recovery between 19 and 23°K increases relative to the total number of defects. These additional close pairs may be produced either by chance, through interstitials coming to rest in sites that in an annealed specimen would have been far from any vacancy and which in a quenched specimen are near to a quenched-in vacancy, or purposely, as one of the processes responsible for the enhancement of defect production in quenched platinum. A short calculation shows that the random process cannot be important.

The amount of resistivity recovered in the temperature interval 19–23°K is about 50% greater in quenched platinum containing a quenched-in vacancy concentration of about  $2 \times 10^{-4}$  ( $\Delta\rho_Q \sim 80 \times 10^{-9}$ ) than in nonquenched platinum when both specimens are irradiated to not more than  $5 \times 10^{14}$  deuterons/cm<sup>2</sup>. This additional resistivity is approximately equal to the additional resistivity injected into quenched platinum above that

injected into annealed platinum during the irradiation. Thus, nearly all of the additional interstitials produced in quenched platinum come to rest on a special set of sites from which they recombine with the quenched-in vacancies within  $21 \pm 2^\circ\text{K}$  ( $0.061 \pm 0.006$  eV). In order for the  $2 \times 10^{-4}$  concentration of vacancies to compete successfully for these interstitials against normal lattice sites on a random selection of sites, each vacancy must have associated with it about 5000 sites at which interstitials are so bound that they combine with the vacancies within the range of energies above. Atomistic calculations show that there are no such number of such sites in the fcc lattice;<sup>25</sup> and, even if there were, the further unrealistic condition would have to be imposed that no more than one interstitial could occupy the group of special bound sites pertaining to only one vacancy.

In an earlier paper<sup>10</sup> we put forward a model for enhanced defect production based on directed defocussing of collision sequences at quenched-in defects. This model proposed that the extra defects are specifically produced at the quenched-in defects. These vacancies then do not need impossibly large capture cross sections since they no longer compete with the entire lattice. The positions of the extra defects relative to the defocussing defects depend upon the energy of the interacting focussons. Under the conditions of these irradiations sites with an activation energy of recombination of about 0.065 eV are most favored.

The earlier paper left unanswered the question as to the particular defect at which defocussing with enhancement of defect production takes place. Figure 9 sheds light on that problem. Since the amount of enhancement below 23°K is very small for the smallest quenched-in vacancy concentration and increases rapidly with increasing vacancy concentration, the particular defect responsible for enhancement of close pair recovery appears to be a multivacancy. There is no evidence in quenched platinum for significant concentrations of larger clusters than divacancies, so we propose that the enhanced defect production in quenched platinum irradiated with 20 MeV deuterons arises from the directed deflections of focussons at quenched-in divacancies.

This model explains why the vacancies produced during an irradiation do not enhance production as do quenched-in vacancies. During an irradiation with 20 MeV deuterons most of the vacancies are produced one at a time, multiple ejections of lattice atoms are very rare. Since vacancies are immobile at the bombardment temperature, multiple vacancies are produced only by successive ejections of atoms from adjacent lattice sites. Neglecting clusters larger than two, the concentration of vacancy pairs,  $C_2$ , is given by

$$C_2 = \int_0^C p(C) dC. \quad (1)$$

<sup>24</sup> A. Sosin and K. Garr, *Bull. Am. Phys. Soc.* **10**, 1179 (1965).

<sup>25</sup> R. A. Johnson, *Bull. Am. Phys. Soc.* **12**, 412 (1967).

In this expression  $C$  is the instantaneous vacancy concentration and  $p(C)$  is the probability that the next vacancy is produced next to an existing vacancy. It is the product of the concentration of sites next to vacancies that are occupied by atoms,  $12(1-C)C$ , and the ratio of cross section for interstitial formation at such a site to the mean cross section. Since atoms near vacancies are less tightly bound this ratio is greater than unity. The maximum energy transmitted to platinum atoms in our irradiations is 450 eV,<sup>26</sup> the displacement threshold energy is 36 eV,<sup>27</sup> and taking the threshold for atoms adjacent to vacancies to be the unrealistically low value of 9 eV a rough calculation of the cross sections yields a ratio slightly less than 2. Thus, an upper limit of the divacancy concentration is

$$C_2 = 12C^2 - 8C^3. \quad (2)$$

For even the largest irradiation injected vacancy concentrations considered in this report,  $L \sim 10^{-4}$ , the divacancy concentration is less than  $10^{-7}$ , too small a concentration to measurably enhance defect production.<sup>10</sup>

Divacancies are much more plentiful following a quench from high temperature. Vacancies remain sufficiently mobile down to some temperature  $T^*$  to maintain equilibrium between single and paired vacancies. Calculations by Doyama<sup>28</sup> show that  $T^*$  is about one-third of the absolute melting temperature ( $T^* \sim 400^\circ\text{C}$  for Pt) for specimens cooling exponentially at the rate used in this work.  $T^*$  decreases as the cooling rate at  $T^*$  decreases. Thus,

$$C_2 = 6C^2 \exp[B/kT^*], \quad (3)$$

where  $B$  is the binding energy of divacancies,  $\geq 0.3$  eV.<sup>5</sup> Then for a quenched-in vacancy concentration of  $10^{-4}$  the divacancy concentration is greater than  $10^{-5}$ .

The stage I annealing peaks are broadened in quenched relative to nonquenched specimens. This can be particularly seen at the  $15^\circ\text{K}$  peak and the valley near  $20.5^\circ\text{K}$ . This broadening further supports our model of production enhancement. The peaks become successively broader as one goes from electron to deuteron to neutron irradiation; i.e., as an increasing fraction of the damage occurs in clusters of defects. Nilan and Granato<sup>29</sup> have shown that strains from nearby defects can produce broadening of close pair annealing substages. Our model predicts that the extra close pairs in quenched specimens are made near other defects so the annealing peaks due to these pairs should be broader than in nonquenched specimens, where

recovery of a greater fraction of close pairs is not affected by strains from other defects.

Finally, our model predicts that recovery of close pairs following irradiation with 2 MeV electrons should be little enhanced by quenching since very few collision sequences are created during such irradiations. The work of Bauer and Goepfingher verifies this prediction.<sup>13</sup> They find that the ratio of the recovery rate in quenched platinum to the rate in nonquenched platinum is never more than a little greater than unity at all temperatures up to  $23.5^\circ\text{K}$ .

### B. Free Migration in Stage I

Recovery between  $23$  and  $28^\circ\text{K}$ , the temperature range immediately above the temperature of maximum annealing rate, is markedly different from recovery below  $23^\circ\text{K}$ . The amount of recovery, below  $23^\circ\text{K}$  is increased by quenching; above  $23^\circ\text{K}$  there is the same amount of recovery in quenched as in nonquenched specimens. This is shown in Table VI for several pairs of specimens that had received nearly identical deuteron fluxes.<sup>30</sup> Below  $23^\circ\text{K}$ , the temperatures of maximum annealing rate in the several substages are not changed by quenching or varying the dose; but above  $23^\circ\text{K}$  recovery is shifted to lower temperature by quenching or increasing the dose. This can be easily seen in Figs. 3 and 4.

These temperature shifts are qualitatively what would be expected for a recovery process due to long range migration of an interstitial type defect as has been postulated for recovery state  $IE$  in copper, for example. Increasing the vacancy concentration by quenching or increasing the dose reduces the number of thermally activated jumps the typical interstitial must make to reach a sink. Even the smallest concentrations of quenched-in vacancies which do not include enough divacancies to increase defect production and recovery below  $23^\circ\text{K}$  contribute measurably to the sink density above that temperature.

For the doses used in this investigation and the purity of these specimens trapping of interstitials at impurities does not appear to be important in the range  $23$ – $35^\circ\text{K}$ . If a significant number of interstitials were trapped, the fractional recovery in the smallest dose specimen would be less than in larger dose specimens because in the former the ratio of impurity traps to vacancy sinks is larger. However, in this work the amount of recovery between  $23$  and  $28^\circ\text{K}$  decreases monotonically from about 13.5% of total damage for the smallest dose to about 10.0% for the largest with unquenched specimens.

<sup>26</sup> F. Seitz and J. S. Koehler, in *Solid State Physics* edited by F. Seitz and D. Turnbull, (Academic Press Inc., New York, 1957) Vol. 2.

<sup>27</sup> W. Bauer and W. F. Goepfingher, *Phys. Rev.* **154**, 584 (1967).

<sup>28</sup> M. Doyama, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson and M. Meshi (Academic Press Inc., New York, 1965) p. 167.

<sup>29</sup> A. V. Granato and T. G. Nilan, *Phys. Rev.* **137A**, 1250 (1965).

<sup>30</sup> The numbers in the last column of Table VI are, in general, not identical. Besides the difficulties in comparing absolute resistivities, these discrepancies arise from the difficulty of separating the end of the close pair recombination from the beginning of the next process;  $23^\circ\text{K}$  is merely a convenient dividing point. Since the processes overlap and since the upper process shifts in temperature with concentration, no one temperature is the best dividing line for all cases.

The recovery rate in the smaller dose specimens remains larger than that in those with larger dose up to 35°K.

The resistivity increment remaining at the end of stage I, about 40% of that added by irradiation in unquenched specimens, is due to interstitials that are immobile at 30°K and the vacancies that these interstitials have not combined with. The quenching experiments prove that most of the immobile interstitial type defects are not di-interstitials (dimers) or larger clusters formed by association of mobile single interstitials since the amount of recovery in the region of free interstitial migration is the same in quenched and unquenched specimens. The large concentration of vacancies in quenched specimens should serve as sinks for most migrating interstitials before the interstitials form stable clusters. We conclude that the interstitial-type defects remaining at the end of stage I are of two classes; one is a second type of interstitial which first becomes mobile at much higher temperature; the other is trapped interstitials. The analysis of stage I recovery that follows indicates that most or all of these immobile interstitials are present at the end of the irradiation. They are created during bombardment probably by dynamic conversion at special sites in the lattice of the type of interstitials mobile in stage I into the type immobile at 30°K. Few or no interstitials are displaced far enough to be converted during electron irradiation following which more than 90% of the damage recovers in stage I.<sup>13</sup> Conversion is much greater during irradiation with heavier particles which give more energy to displaced ions and, correspondingly, stage I recovery is smaller after deuteron or neutron irradiation.<sup>14,15</sup>

If the distribution of mobile interstitials and of vacancies is continuously randomized so that the concentration of interstitials on sites, from which they will combine after one step toward the nearest vacancy, is always the same as the over-all interstitial concentration, then the annealing rate is proportional to the product of the concentrations of vacancies and of mobile interstitials. The rate of change of the observable, resistivity is then

$$d\rho/dt = -K\rho_0IV. \quad (4)$$

In this expression  $K$  is the product of the number of interstitial jumps per unit time by the number of sites near each vacancy from which a jump toward the vacancy results in recombination,  $\rho_0$  is the resistivity added by one Frenkel pair,  $I$  is the concentration of mobile interstitials, and  $V$  the concentration of vacancies. At the beginning of free interstitial migration

$$V = V_I + V_{III} + V_{IV}, \quad (5)$$

where  $V_I$  is the concentration of vacancies that mobile interstitials will combine within stage I,  $V_{III}$  is the concentration of vacancies paired with interstitials that are immobile in state I, and  $V_{IV}$  is the concentra-

tion of quenched-in vacancies. The solution of Eq. (4) is

$$I = v\{[(I_I + v)/I_I] \exp[vKt] - 1\}^{-1}. \quad (6)$$

In this expression  $v$  is  $V_{III} + V_{IV}$  and  $I_I$  is the concentration of interstitials that migrate freely in stage I.

We plot in Fig. 10 recovery curves calculated using Eq. (6) for several values of quenched-in resistivity and two deuteron doses. Resistances were converted to defect concentrations by using  $4 \times 10^{-6}$  and  $6 \times 10^{-6}$  ohm cm for the resistivity increments due to one atomic percent of vacancies and of Frenkel pairs.<sup>27</sup> The activation energy for free migration was taken to be 0.07 eV, the value just above that found for the highest close pair peak, and the vacancy capture cross section and the vacancy capture cross section and attempt frequency were chosen to confine the recovery to the observed temperature range. The calculated recovery curves exhibit qualitatively the temperature shifts that result from quenching or changing the dose; and the change with quenched-in vacancy concentration of the temperature at which the recovery rates in quenched and in not quenched specimens are the same, a quantity that can be determined from Fig. 9, is predicted to better than 10% accuracy by Eq. (6).

Recovery curves calculated from Eq. (6) are only approximate. The requirement of continual randomization is not met. A proper recovery theory should be based on a diffusion limited reaction rather than on chemical rate arguments. However, the available data are not sufficient to calculate the initial distribution of interstitials and vacancies, and the interaction potentials between interstitials and other defects are not well enough known to warrant more detailed treatment.

Equation (6) fits our data much better than does an equation derived from a model in which most interstitials are mobile in stage I; i.e.,  $V_I \gg V_{III}$ . The latter model represents annealing after electron irradiation well<sup>13</sup> but gives recovery curves with much too long high temperature tails in unquenched, as compared to quenched specimens to represent well recovery after deuteron irradiation. When  $V_I \gg V_{III}$  the shifts with changes of quenched-in vacancy concentration of the temperature at which the ratio of recovery rates in quenched and in unquenched specimens is unity are much greater than observed. Further, since the amount of recovery in this temperature range is not changed by quenching, we conclude that all of the interstitials that are mobile in this range are annihilated and none are converted. Conversion, if it occurred, would be suppressed by excess quenched-in vacancies resulting in more recovery in quenched specimens. Conversion and trapping are not important in stage I recovery because of the sizable fraction of immobile interstitials present throughout this stage giving an excess of vacancies over mobile interstitials, traps, or conversion sites.

Above 23°K the annealing rate in the larger dose specimen of two unquenched specimens or in the

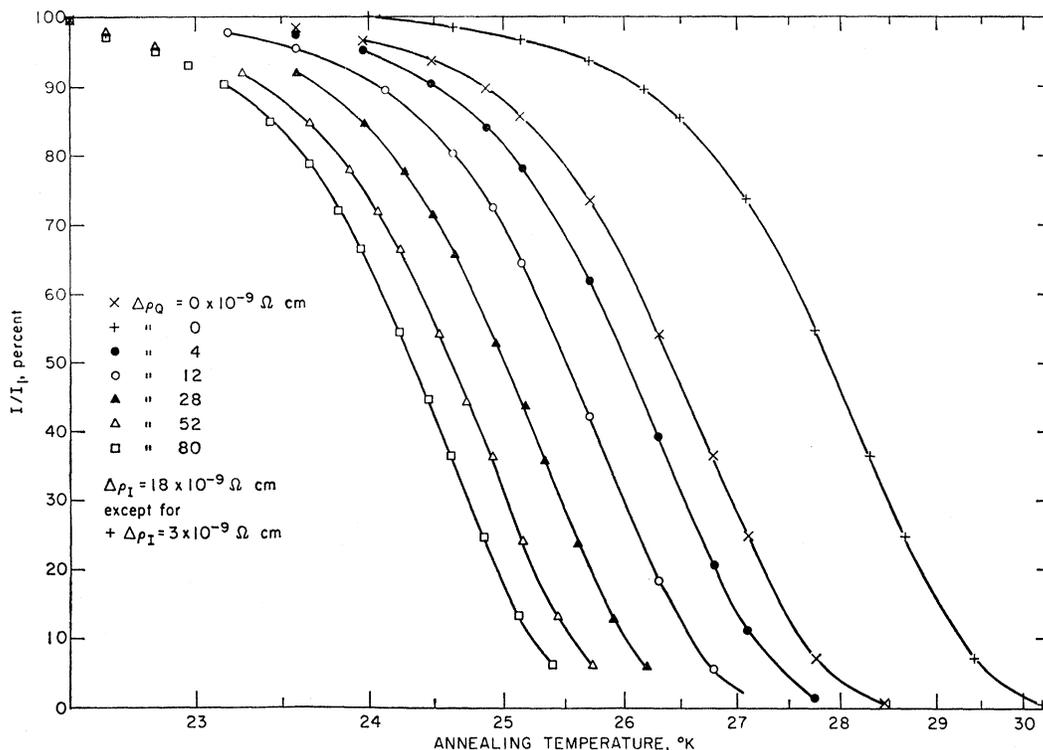


FIG. 10. Isochronal annealing curves calculated from Eq. (6). The symbols are computational points included to identify the various curves.

quenched of two specimens given equal deuteron dose is first larger then smaller than the rate in the smaller dose or unquenched partner (Figs. 4 and 6). These shifts in annealing rates are most naturally interpreted as indicating a decrease with increasing sink density of the temperature of maximum annealing rate due to interstitial free migration. The approximation of Bauer and Sosin<sup>23</sup> gives a temperature shift of about 2°K for the dose ratio of 8½:1 of the two pairs in Fig. 4. The temperature of maximum annealing rate cannot be experimentally found because of overlap with close pair recombination; but the change of this temperature with dose must be somewhat less than the 3°K difference between the temperatures of steepest fall and rise in Fig. 4. All vacancies are potential sinks for mobile interstitials, so the temperature shifts do not depend on the fraction of interstitials that are mobile in stage I. The temperature shifts are further evidence for interstitial migration but are not sensitive to the ratio  $V_I/(V_I+V_{III})$  since  $V_{III}$  is nearly proportional to  $V_I$ .

There is similar agreement for temperature decreases in long range migration of interstitials to sinks when quenched-in vacancies contribute to the sink density. Dose dependence is not so straightforward in quenched specimens. Because of extensive radiation annealing, the defect distribution in very low-dose specimens is different from that in specimens given doses an order of magnitude larger.

Alternatively, von Jan has argued that in no fcc metal are interstitials mobile in stage I.<sup>31</sup> However, his arguments neglect the evidence for interstitial migration at the end of stage I afforded by doping experiments which show that certain impurities suppress this recovery by trapping mobile interstitials before they combine with vacancies<sup>1,2</sup> and by measurements of modulus changes which show that an entity, different from a vacancy, migrates to and pins dislocations at the end of stage I.<sup>32</sup>

Our data strongly suggest that von Jan's model does not apply to platinum either. The dose dependence of the ratio of recovery rates between 23 and 30°K can be, as shown above, explained on the basis of a free migrating interstitial. To simulate such behavior by close pair recovery requires several first-order processes of different energy in this range; but anneals with temperature increments as small as 0.25°K do not show such structure.

### C. Recovery Above Stage I

The small, nearly featureless recovery in stage II is of much different character from that in stage I. Our results can best be explained on the basis of escape of interstitials from a range of traps through stage II and their subsequent annihilation as in the similar stage

<sup>31</sup> R. von Jan, Phys. Status Solidi 17, 361 (1966).

<sup>32</sup> D. W. Keefer, Acta Met. 13, 1135 (1965); 14, 1409 (1966).

TABLE VII. Percent of damage added by irradiation remaining near 300°K.

Run and $T_F$ °K	$\Delta\rho_I$ ohm cm $\times 10^{-9}$	$\Delta\rho_Q$ ohm cm $\times 10^{-9}$	$\Delta\rho(T_F)/\Delta\rho_I$ percent
9 300°K	1.61	0	3.7
	1.77	77.5	-11.0
	14.15	0	14.5
	15.85	11	4.1
	16.7	17	2.75
13 296°K	15.6	52	-4.7
	15.1	0	15.6
8 295°K	17.4	3.5	9.1
	3.5	0	10.8
4 300°K	25.2	0	15.95
	117.1	0	20.15
	120.4	52	14.0

in aluminum. Since the trapping of interstitials is not important during stage I recovery we further require that most of the trapped interstitials were trapped during the irradiation. The similarities in the recovery spectrums of high- and low-dose and quenched and unquenched specimens come about naturally on this model since in all cases interstitials escape from the same traps. The greater displacements given to interstitials with deuteron irradiation as compared to electron irradiation allow a greater proportion of interstitials to be trapped in the former just as more are converted to stage III interstitials since both trapping and conversion depend upon a displaced interstitial reaching one of certain special classes of lattice sites well removed from the vacancy where it came from.

The reduced fraction of recovery in stage II for low-dose as compared to high-dose specimens implies that the ratio of displaced interstitials converted to stage III interstitials to those trapped decreases with increasing dose. The mean range of displaced interstitials (focusons) also decreases with dose because radiation damage reduces the lattice regularity that makes long range transport possible. Conversion, a process in which the focuson must interact at a particular site with considerable energy, also falls off with decreasing range since the typical focuson passes fewer sites with the requisite energy. On the other hand, trapping, a process in which the focuson arrives at the trapping site near the end of its range, should be almost independent of range. Recapture at deeper traps after release from shallow traps is not important since the ratio of the relative recovery rates of small to large dose specimens decreases with increasing annealing temperature in stage II.

The presence of a large number of quenched-in vacancies favors the release of interstitials from traps earlier in stage II than for unquenched specimens; but the total amount of recovery in stage II is very little changed by quenching. The number of trapping sites (principally sites near impurity atoms) is not changed much by the extra vacancies but the escape of trapped interstitials and their annihilation is accelerated by the presence of nearby vacancies.

Stage III recovery in platinum, 240–350°K, has several striking features. Recovery in all low-dose specimens, quenched and not quenched, is much greater than in corresponding specimens given larger doses so that in low dose, quenched specimens recovery becomes greater than 100% of damage; and, at least for the largest doses and subject to the problems described in a previous section involved with measuring this stage to completion, the amount of recovery is increased by the presence of quenched-in vacancies.

Earlier studies of recovery of deformed platinum<sup>22</sup> have shown that recovery in this temperature range is due to the long range migration of an interstitial type defect with an activation energy of 0.7 eV. Recent work on neutron-irradiated platinum<sup>33</sup> has confirmed that an interstitial is mobile in stage III. It is known from quenching studies that vacancies are immobile below 450°K and, indeed, some of the quenched specimens used in the investigations reported in this paper were aged at 373°K before irradiation without changing damage production or recovery in the subsequent irradiation and anneal from that in quenched, unaged specimens.

The strong dependence on dose of this recovery shown by the measurements at 300°K and listed in Table VII are evidence for a trapping mechanism that increases rapidly in effectiveness with dose. This is readily achieved for quenched specimens if stage III interstitials form stable clusters; because as the dose increases, the ratio of mobile interstitials to vacancy sinks increases, which increases the probability that an interstitial will encounter another interstitial and nucleate a cluster before it recombines with a vacancy. In unquenched specimens the picture is not so straightforward. If the defect distribution were completely random and if interstitials could only annihilate at vacancies or cluster at other interstitials, then changing the dose would not change the ratio of annihilations to clusterings. However, neither of these assumptions is true. Stage III interstitials have in general been considerably displaced from their original site before being converted so that vacancy rich and interstitial rich regions are not identical. Interstitials in platinum can also annihilate at grain boundaries and dislocations that have recently moved and, in analogy with interstitials in copper, they probably migrate to and then along grown-in dislocations to form pinning clusters. All of these perturbations to the assumptions above favor increased interstitial clustering with increasing dose.

The very great increase produced by quenching in the magnitude of stage III recovery in the specimens given the largest doses follows naturally from this picture. The quenched-in vacancies suppress clustering which would otherwise be particularly important in these specimens.

<sup>33</sup> J. M. Galligan and M. J. Attardo, Bull. Am. Phys. Soc. 13, 302 (1967).

The resistivities of specimens, quenched before irradiation to give a resistivity increment greater than  $50 \times 10^{-9}$  ohm cm and irradiated to a further increment smaller than  $20 \times 10^{-9}$  ohm cm, are reduced to less than the preirradiation value by an anneal at 300°K. This is shown in Table VII. Since interstitials and vacancies are produced in equal numbers during irradiation complete removal of all interstitials must leave at least as many vacant lattice sites as existed before irradiation. The measurements show that the mean resistivity increment per vacant site of the defects existing after irradiation and anneal at 300°K is less than it was before irradiation. This must be accomplished by changing the distribution of the vacancies. Our model for enhanced defect production rates in quenched platinum predicts that interstitials are preferentially created near divacancies and recombination of the interstitial-divacancy complex results in the replacement of one divacancy by two single vacancies. If the resistivity increment at 4.2°K of two single vacancies is less than that of one divacancy then our observation would follow. Measurements on quenched gold indicate that, at least in that metal, the divacancy does have greater resistivity than two single vacancies.<sup>34</sup>

All of the resistivity added by quenching<sup>5</sup> and the remainder of the resistivity added by irradiation recover in one final stage, Stage IV. This is also the largest recovery stage after plastic deformation.<sup>22</sup> With the information gained from quenching experiments this is the easiest of all stages to understand. Quenching introduces only one type of defect, the vacancy, into platinum. When platinum supersaturated with vacancies is held at any temperature at which vacancies have appreciable mobility the vacancies diffuse to and are annihilated at a set of sinks most of which existed before the anneal began. There is no evidence for clusters larger than divacancies. Essentially all of the extra resistivity from quenching disappears in the course of an isothermal anneal at any temperature above 200°C. The final recovery stage in irradiated platinum behaves the same on the evidence of this report and others.<sup>20,35</sup> This recovery, too, is due to the diffusion of mobile

vacancies to sinks. Among the sinks after irradiation, however, are also clusters of interstitials. These clusters, when reduced by vacancy capture to below a critical size, diffuse rapidly to sinks. Because of the resistivity changes when specimens are remounted for anneals above 300°K, our data do not tell if the resistivity removed in stage IV is just equal to that quenched in, is greater because some interstitial annihilation is postponed to this stage, or is less because of divacancy breakup during earlier annealing.

No recovery stage V corresponding to the final stage seen after plastic deformation has been found after irradiation of platinum. This is further evidence that mobile vacancies in platinum do not form stable clusters, and that all interstitial clusters are removed in stage IV.

### SUMMARY

The work discussed in this report, particularly the careful comparison of nonquenched with quenched specimens, leads us to the following conclusions:

1. Defects are produced by the interaction of focusons with divacancies that would not have been produced in the absence of divacancies.
2. Recovery below 23°K is due to close pair recombination.
3. The extra interstitials produced as in item 1 recover by close pair recombination.
4. An interstitial migrates freely with an activation energy of 0.07 eV at the end of stage I.
5. Stage II recovery is due to the annihilation of interstitials released from traps by thermal agitation.
6. A second type of interstitial is mobile in stage III with an activation energy of 0.7 eV.
7. These stage III interstitials can form clusters stable up to at least 450°K.
8. Vacancies and divacancies are first mobile in stage IV.

### ACKNOWLEDGMENTS

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<sup>34</sup> M. Meshii, T. Mori, and J. W. Kauffman, *Phys. Rev.* **125**, 1239 (1962).

<sup>35</sup> G. R. Piercy, *Phil. Mag.* **5**, 207 (1960).