Comparison of Defects Injected into Platinum by Quenching and by Radiation Doping*

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Specimens made from pure, well-annealed platinum, from quenched platinum, and from platinum that had been previously irradiated below 100°K and annealed to above room temperature were bombarded simultaneously below 7°K with 20-MeV deuterons. Damage production and recovery in the three types of specimens were compared in detail. Both of the preirradiation treatments increase the sink density for interstitials mobile in stage I. The initial defect production rate is increased by the presence of vacancy clusters and decreased by the presence of interstitial clusters.

I. INTRODUCTION

MUCH information about the properties of defects injected into metals during irradiation can be gained by studying the effects of excess lattice vacancies on the production and recovery of such defects. Three of the problems that have been studied with this technique concern the temperature of long-range interstitial migration, the proportions of various types of defects produced by the irradiation, and the mechanism of radiation annealing. The uses of vacancies in investigations of these problems are discussed in the next three paragraphs.

In close-packed metals the interstitial is the more mobile member of a Frenkel pair. Vacancies injected into the metal before the irradiation serve as sinks for interstitials produced during an irradiation at temperatures so low that no defects are mobile. These additional sinks, over and above those provided by the vacancies produced during the irradiation, first become important during an annealing process in which mobile interstitials sample a representative portion of the lattice before reaching a sink. The duration of such a process can be determined by comparing after identical irradiations recovery of specimens well annealed before irradiation with recovery of specimens containing excess vacancies. Studies of this type have been carried out by Bauer and Sosin[1] in gold and by Jackson and Herschbach[2] in platinum.

If the concentration of vacancies before the irradiation is sufficiently large and the specimen is irradiated at a temperature that lies in the region of stage II, then almost all of the interstitial-type defects that are mobile in stage I will recombine with vacancies during the irradiation. Only those interstitials that are trapped at impurities or are converted into a type of interstitial first mobile in stage III will remain after the irradiation. The instantaneous concentration of stage-I interstitials will be at all times too small for clustering of these defects to be important. From such experiments an upper limit can be set to the number of stage-III interstitials produced during the irradiation. Information is also gained about trapping sites for interstitials. Experiments of this type have been carried out by Duesing *et al.*[3]

Some models of radiation annealing, the decrease in defect production with increasing defect concentration, are based upon the nonthermal recombination of newly created interstitials (vacancies) with nearby, previously produced vacancies (interstitials).[4–6] When such recombinations are the most important perturbation to production, the rate of increase of Frenkel pairs approaches

$$dN/dt = A(1-2vN). \quad (1)$$

In this expression, N is the concentration of Frenkel pairs, A is the concentration made in unit time, and v is the number of atomic sites around a defect in which nonthermal recombination takes place. Equation (1) holds strictly only for vanishingly small N; in general, one must consider higher-order terms in N which represent the change in the number of lattice atoms with increasing defect concentration and which take account of the nonuniform distribution of defects. Since the maximum value of N reached in experiments to date is about 10^{-3}, these additional terms are small. The rate of change of Frenkel pairs is identical to the rate of change of interstitials which, on this model, decreases linearly with the concentration of vacancies; so, in a specimen which contained a concentration V_0 of vacancies before

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[1] W. Bauer and A. Sosin, Phys. Rev. **136**, 255 (1964).

[2] J. J. Jackson and K. Herschbach, Phys. Rev. **164**, 951 (1967).

[3] G. Duesing, H. Hemmerich, D. Meissner, and W. Schilling, Phys. Status Solidi **23**, 481 (1967).

[4] G. Burger, H. Meissner, and W. Schilling, Phys. Status Solidi **4**, 281 (1964).

[5] M. Balarin and O. Hauser, Phys. Status Solidi **10**, 475 (1965).

[6] F. Dworschak, Chr. Lehmann, H. Schuster, H. Wollenberger, and J. Worm, Brookhaven National Laboratory Report No. BNL 50083, 1967 (unpublished).

the irradiation, this rate is given by

$$(dN/dt)_{V_0}=A_{V_0}[1-v(2N+V_0)], \qquad (2)$$

where A_{V_0} is the concentration of interstitials made in unit time with V_0 excess vacancies. To first order in vN, the ratio of the rates from Eqs. (2) and (1) is

$$\frac{(dN/dt)_{V_0}}{dN/dt}=\frac{A_{V_0}}{A}(1-vV_0). \qquad (3)$$

By measuring this ratio in specimens with different values of V_0, the validity of the above model for radiation annealing can be examined, a value given for v, and the effect of defects on production rates determined. Such experiments have been performed by Swanson and Piercy[7] in gold and by Herschbach and Jackson[8] in platinum.

In close-packed metals, the thermal-equilibrium concentration of lattice vacancies is orders of magnitude greater than the equilibrium concentration of interstitial atoms at all temperatures below the melting point. The atomic fraction of vacancies at the melting point lies between 10^{-4} and 10^{-3} in many fcc metals,[9] and by rapid quenching most of these vacancies can be retained in supersaturation at low temperature; so, by a proper choice of quench conditions, a wide range of vacancy concentrations free from other defects can, in theory, be injected into the lattice before irradiation. However, most metals are contaminated when carried through a quench cycle. In addition to gold, aluminum, and platinum, only silver and tungsten have been quenched without picking up so many impurities that vacancy interactions are seriously perturbed.[10]

Vacancies can be injected into metals nonthermally by plastic deformation and by irradiation. These treatments introduce other types of defects in addition to vacancies, but by selective annealing all defects more mobile than vacancies can be removed. Plastic deformation produces interstitials, vacancies, and dislocations, and the latter are removed in significant numbers only at temperatures above those at which recovery of vacancies takes place. The damage produced by low-temperature irradiation with charged particles lighter than the lattice atoms consists almost entirely of Frenkel pairs. Interstitial-type defects such as single interstitials and perhaps very small interstitial clusters are more mobile than single vacancies and can be entirely eliminated without complete removal of the vacancies. Larger interstitial clusters are less mobile than vacancies, but the number of such clusters is smaller than the number of vacant lattice sites by a factor greater than n', the smallest number of interstitials in a stable cluster. The existence of recovery stage IV in most metals proves that some vacancy-type defects remain when all interstitial-type defects of size smaller than n' have been eliminated. A further discussion of these points can be found in Corbett's review article.[11]

Since vacancies free from contaminants can be injected into only a few metals by quenching, and since some of these few must be held below room temperature between the quench and the subsequent irradiation to prevent clustering of the vacancies, many investigations have been made using specimens into which vacancies had been injected by a low-temperature irradiation followed by a partial anneal. Some instances are given in Refs. 12–15.

Platinum is a metal into which excess vacancies can be injected successfully by both techniques; and we have taken advantage of this to compare the effects of quenched-in vacancies with those of vacancies introduced by a low-temperature irradiation followed by a partial anneal on defect production in a subsequent irradiation and on recovery of these defects. Because of the relatively high injection temperatures used to dope platinum thermally with vacancies, the quenches in still gases required for the thin samples used in charged-particle irradiations are rapid enough to retain vacancy concentrations comparable with those from the best quenches into liquids. The quenched state in platinum is stable at room temperature, which facilitates handling of the quenched specimens before irradiation. Recovery after quenching is much simpler in platinum then in aluminum or the noble metals; this indicates that formation of quasistable vacancy clusters is not important.[16] With respect to vacancies remaining after irradiation and partial anneal, measurements following irradiations with either electrons[17] or deuterons[2] show the existence of a distinct recovery stage, stage IV, which occurs in the same temperature range as does the one recovery process after a quench. This proves that lattice vacancies remain after all mobile interstitials are removed. In addition, stage IV in platinum is well separated from the other recovery stages, so that all defects more mobile than vacancies or divacancies can be removed with no appreciable migration of the latter.

[7] M. L. Swanson and G. R. Piercy, Can. J. Phys. **42**, 1605 1964).

[8] K. Herschbach and J. J. Jackson, Phys. Rev. **153**, 689 (1967).

[9] R. O. Simmons, in *Radiation Damage in Solids*, edited by D. S. Billington (Academic Press Inc., New York, 1962), p. 568.

[10] See preface and articles in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshil (Academic Press Inc., New York, 1965).

[11] J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Suppl. 7.

[12] J. W. Corbett, Phys. Rev. **137**, A1806 (1965).

[13] H. I. Dawson, G. W. Iseler, and J. W. Kauffman, in *Lattice Defects and Their Interactions*, edited by R. R. Hasiguti (Gordon and Breach, Science Publishers, Inc., New York, 1967).

[14] J. W. Kauffman, C. L. Snead, Jr., and F. W. Wiffen, Bull. Am. Phys. Soc. **12**, 301 (1967).

[15] K. Herschbach and J. J. Jackson, Phys. Rev. **158**, 661 (1967).

[16] J. J. Jackson, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshil (Academic Press Inc., New York, 1965), p. 467.

[17] W. Bauer and A. Sosin, Phys. Rev. **147**, 482 (1966).

TABLE I. Specimen preparation and irradiation data. *A* represents annealed; *Q* represents quenched with the resistivity increment from quench as given. Specimens 1 and 4 were shielded during doping irradiations 6I and 10I.

Irradiations with doses (deuterons/cm²)	Position of specimen	Treatment before irradiation (See notes)	Doping irradiation: Resistivity increment (10^{-9} Ω cm)	Doping irradiation: Remnant after 300°K anneal (%)	Test irradiation: Resistivity increment (10^{-9} Ω cm)
6I	1	*Q* 86.5	(0.4)	(−25)	18.6
145×10^{14}	2	*Q* 50.2	25.3	Specimen	Broken
	3	*Q* 86.5	14.7	28	17.2
6	4	*A*	(0.8)	(37)	15.2
22×10^{14}	5	*A*	39.2	58	14.2
	6	*A*	39.9	58	14.5
10I	1	*Q* 28.0	(0.9)	(22)	15.7
342×10^{14}	2	*Q* 9.5	94.7	39	14.5
	3	*A*	102.1	46	14.3
10	4	*A*	(1.6)	(25)	14.9
22×10^{14}	5	*A*	106.7	46	14.2
	6	*Q* 28.0	79.2	27	15.4

II. EXPERIMENTAL

The specimens were made from platinum wire, 0.002 in. in diam, annealed and purified as described in a previous report.[18] The annealed specimens used in this work had a resistivity at 4.2°K of $(3.8\pm0.3)\times10^{-9}$ Ω cm. About half of this residual resistivity arises from electron scattering from the cylindrical surface of the specimen[19]; the remainder of the resistivity corresponds to an impurity concentration much less than 1 ppm.

The quenched specimens were prepared from the annealed material described above. Wires long enough that a length sufficient for at least four specimens (5 in.) was within 10°C of the mean quench temperature were heated to the quench temperature in still air at 40 psi by the passage of electric current. The mean temperature of the wire was calculated from the increase in its electrical resistance, and temperature uniformity was checked with an optical pyrometer. The wires were quenched by abruptly reducing the heating current to less than 3% of the value needed to maintain the specimen at the elevated temperature.[2]

Specimens irradiated in the annealed condition were prepared by subsequently annealing sections of the quenched wire. The residual resistivity of these specimens was the same as it had been before the quench. Details of the specimen preparation are given in Table I.

The specimens were irradiated with 22-MeV deuterons from the Argonne 60-in. cyclotron. The cryostat and auxiliary equipment have been described previously.[20] Six specimens can be irradiated and annealed simultaneously in this cryostat, and two of the specimens, those in positions 1 and 4, can be shielded behind a movable shutter during the doping irradiations. Two doping irradiations were performed, 6I, during which the specimen holder was at 77°K, and 10I with the holder at 6°K. Heating by the deuteron currents ($\sim4.5\times10^{12}$ d/cm² sec) used in the doping irradiations raised the specimen temperature in each of these irradiations to about 20°K above that of the specimen holder. Following each doping irradiation, the specimens were allowed to warm to room temperature, where they remained for several days. This treatment removes most of the defects mobile in stage III that were injected during the doping irradiations[2] but does not affect the resistivity of any of the specimens that were not irradiated.[16] The resistivity of the shielded specimens increased slightly during the doping irradiations because of damage from neutrons created during these irradiations. After the room-temperature anneals, the shutter was opened. The specimen holder was cooled to 4.2°K, and the test irradiations 6 and 10 were given. The deuteron current during these irradiations was held below 3×10^{11} d/cm². Previous investigations have shown that the temperatures of all specimens used in these irradiations remain below 7°K with such a beam current.

Although the total deuteron flux through the specimen chamber was measured continuously during bombardment, the exact deuteron flux at the position of each specimen could not be measured. Before each test irradiation, the beam was adjusted so that a radiograph showed it to be uniform over an area larger than that subtended by the specimens. The beam need not necessarily remain uniform throughout the irradiation, and damage-production data from other bombardments indicate that it has not always done so[8]; but we believe that there were no large fluctuations during test irradiations 6 and 10 because the damage in all specimens increased smoothly with dose. A highly focused beam was needed to perform the doping irradiations in reasonable time. This beam was continually swept across the specimens, but variations in deuteron flux through the specimens were probably greater than during test irradiations. For all irradiations, however, the pairs of specimens in positions n and $n+3$ ($n=1$, 2, or 3) receive nearly identical fluxes.[8]

[18] J. J. Jackson, in *Realstruktur und Eigenschaften von Reinststoffen*, edited by E. Rexer (Akademie-Verlag, Berlin, 1967), Vol. III, p. 659.

[19] R. P. Huebener, Phys. Rev. **140**, A1836 (1965).

[20] K. Herschbach, Rev. Sci. Instr. **37**, 171 (1966).

The damage was measured by the increase in residual resistivity of the specimens. On any given specimen, changes in resistance could be measured reproducibly to within 3×10^{-7} Ω. In a typical specimen with a room-temperature resistance of about $1\frac{1}{2}$ Ω, this corresponds to a change of 2×10^{-12} Ω cm in resistivity. However, the length of specimen that subtends the deuteron beam is not known to much better than 5%, so that absolute resistivity changes in the irradiated section are uncertain to that degree.

The annealing procedure was the same as in most other work that we have reported.[15] All specimens in an irradiation were pulsed together to a monotonically increasing series of annealing temperatures, held at each annealing temperature for 10 min, and after each isochronal anneal returned to 4.2°K for measurement of the residual resistance. All specimens that were irradiated together received identical thermal treatment during the anneal.

III. RESULTS

A. Defect Production

The changes in resistivity resulting from the doping irradiations, the anneals at room temperature, and the test irradiations are shown in Table I. In order to show the effects of the various treatments on radiation annealing (the decrease in defect production rate with dose), the rate of resistivity increase per unit deuteron flux in several specimens is plotted as a function of dose over the range of the test irradiations in Fig. 1 and to much larger doses in Fig. 2.

The absolute values of the resistivity changes are uncertain to the extent discussed in the previous section, but relative changes in resistivity increment per unit deuteron flux between specimens at n and $n+3$

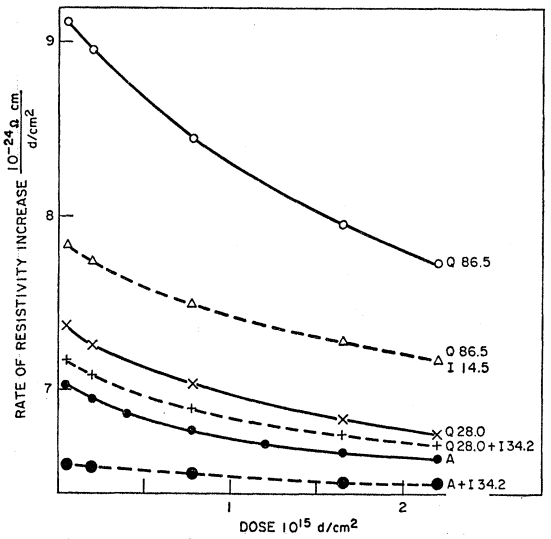

FIG. 1. Effect of various treatments on the rate of resistivity increase as a function of deuteron dose.

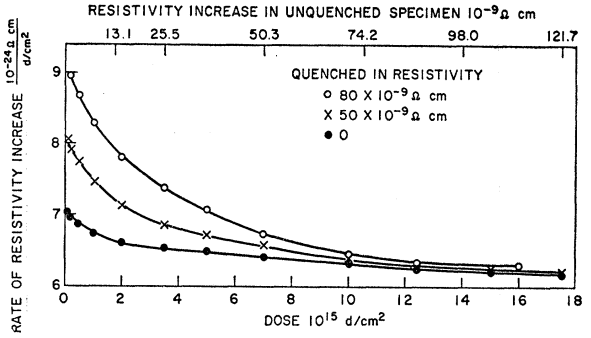

FIG. 2. Rate of resistivity increase at large deuteron doses in quenched and in untreated platinum.

are certain to better than 1%. Of necessity, it is impossible that a doped specimen and a shielded specimen be located in positions n and $n+3$, but the agreement between resistivity changes in identical specimens such as irradiation 6, Nos. 5 and 6, and irradiation 10, Nos. 3 and 5, indicates that beam inhomogeneities were small during these bombardments. Under such conditions, relative changes between all pairs can be compared with good accuracy.

In all of the specimens, the defects injected by the doping irradiation that survive the anneal at room temperature reduce both the initial rate of resistivity increase $(d\rho/dF)_{F=0}$ and the amount of radiation annealing $(d\rho/dF)_{F=0}-(d\rho/dF)_F$ during the subsequent test irradiation. F is the radiation dose given to the specimens (deuterons/cm²). The magnitude of these reductions is greatest for the specimens with the largest concentration of quenched-in vacancies, the specimens that, when undoped, have the largest value of $(d\rho/dF)_{F=0}$. The test irradiations of doped specimens resemble segments of irradiations to much longer total dose, these segments beginning at some positive value of F. For example, the resistivity increments in the test irradiations of doped, unquenched specimens are similar to the increments that result from equal doses lying between $2\frac{1}{2}$ and 5×10^{15} d/cm² in the high-dose curves of Fig. 2.

The data plotted in Fig. 2 show that both the resistivity added per incident deuteron and the rate of change of this quantity decrease as a function of total deuteron flux; that is, $d(d\rho/dF)/dF$ is negative and $d^2(d\rho/dF)/dF^2$ is positive. These results agree qualitatively with the findings of other workers.[4–6] These data also show that for doses giving resistivity increase in an unquenched specimen greater than about 60×10^{-9} Ω cm, quenched-in vacancies have negligible effect on $d\rho/dF$. This result was also seen in a third irradiation to a total dose of 22×10^{15} d/cm², in which beam fluctuations were too great to determine $d\rho/dF$ for each specimen, but in which the fluctuations affected the quenched and unquenched specimens equally. Here, too, $(d\rho/dF)_q-(d\rho/dF)_{n.q.}$ became very small in the latter stages of the irradiation.

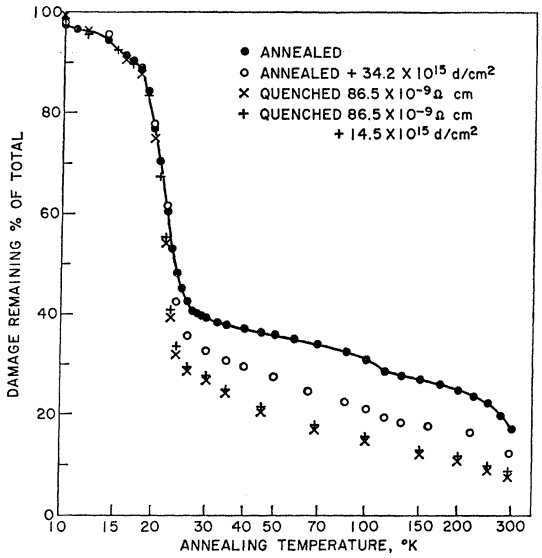

FIG. 3. Recovery after deuteron irradiation of quenched, of radiation-doped, and of untreated platinum.

During the doping irradiations, the resistivity increments in the quenched specimens were less than in annealed specimens. This is to be contrasted with the results of the test irradiations of this series and all other irradiations that we have performed for which the resistivity increment increased with quenched-in-vacancy concentration.[2] The specimen temperatures during both doping irradiations were above 25°K; during all previous irradiations, they have been below 15°K. This is strong evidence that a type of interstitial becomes mobile and migrates through the lattice at some temperature above 15°K and below the specimen temperature during doping irradiation No. 10.

B. Recovery in Stage I

The annealing of the resistivity injected during a test irradiation is shown in Fig. 3. There are four curves in this figure, one for a specimen in each of the four possible preirradiation states: annealed, quenched, annealed then radiation-doped, and quenched then radiation-doped. The rate of change of these recovery curves is plotted as a function of stage-I annealing temperature in Fig. 4. Such plots give an over-all view of recovery, but to emphasize the effects of the various treatments on recovery it is necessary to display the data in a way that takes better advantage of the simultaneous bombardment and identical annealing of several specimens. One such method is the ratio plot devised by Sosin and Garr[21] in which the ratio of recovery rates in specimens annealed together is plotted against the annealing temperature. These ratios are not sensitive to small errors in the temperature or duration of the annealing pulses. In Fig. 5, we give the ratios of the normalized stage-I recovery rates of quenched, of radiation-doped, and of quenched and radiation-doped specimens to the well-annealed specimen in test irradiation 6. The ratios for similar combinations from irradiation 10 are plotted in Fig. 6. The rates are normalized by dividing the resistance changes of each specimen by the resistance injected into that specimen during the test irradiation. Thus, if the ratio of a pair of specimens differs from unity in an interval, then the proportion of resistivity due to defects interacting in that interval to the total resistivity increment from irradiation has been changed by the treatment.

Nearly 60% of the total resistivity injected into untreated platinum specimens recovers in stage I between 10 and 30°K. This interval is marked by four distinct recovery peaks. Another recovery process is indicated by the hump on the high-temperature side of the largest peak, but this process has not been resolved.[2,22] In quenched specimens, this hump moves into the peak and the dip between the two largest peaks is filled. Various studies have shown that below 23°K recovery is by correlated close-Frenkel-pair recombination, and above that temperature recovery is by random migration of interstitials to vacancy sinks.[2,23]

None of the three treatments considered in this report has much effect on recovery below 18°K. This is in agreement with other data and with the belief that such recovery is due to the recombination of very close

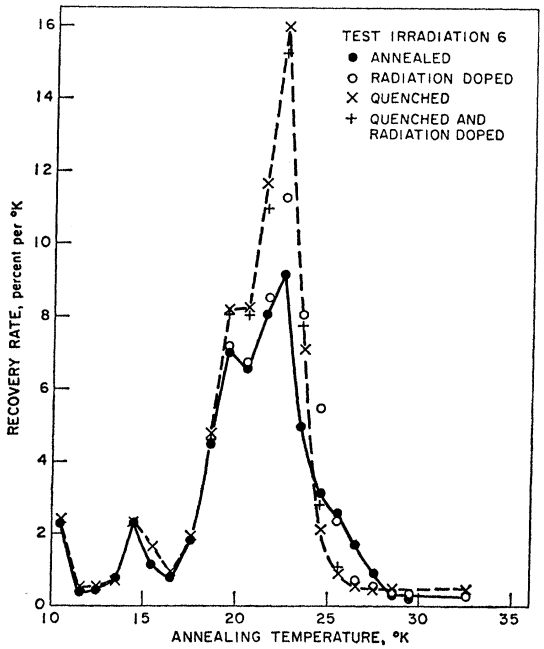

FIG. 4. Slope of the recovery curves in stage I of specimens given different treatments before irradiation but identical thermal histories during annealing.

[21] A. Sosin and K. R. Garr, Phys. Rev. **161**, 664 (1967).

[22] R. R. Coltman, C. E. Klabunde, and J. K. Redman, Phys. Rev. **156**, 715 (1967).

[23] W. Bauer and W. F. Goeppinger, Phys. Rev. **154**, 588 (1967).

pairs.[24] The ratios of the recovery rates of quenched to unquenched specimens are substantially larger than unity in the interval 19–23°K. The extra resistivity recovered in this interval is equal to the extra resistivity injected into the quenched specimens by the irradiation. This is true not only for the conditions of this investigation, but also for a wide range of Frenkel-pair and vacancy concentrations.[2] There is only a very little enhancement of fractional recovery between 19 and 23°K in the unquenched, radiation-doped specimens. These also had a smaller resistivity increment than did annealed specimens in the test irradiations, so that, within the limits of our measurements of absolute resistivities, radiation doping does not change the amount of resistivity recovery in this interval. The enchancement of recovery between 19 and 23°K in quenched specimens is reduced absolutely and relative to total damage by radiation doping.

In the next temperature interval, 23–28°K, the last in which the recovery rates are large enough to compare meaningfully over-1°K increments, ratio plots of all treated versus untreated specimens are similar. At the beginning of this interval, annealing proceeds much faster in the treated specimens; later, the annealing rate is greater in the untreated ones. This gives the ratio plots an S shape which is characteristic of recovery of a pair of specimens one of which contains a greater density of sinks for the defect that is mobile in this temperature range. Both treatments, quenching and radiation doping, increase the sink density. The amount of resistivity recovered in this interval is the same in the quenched as in the untreated specimens, given the same deuteron dose. Again, this has been corroborated over a wide range of concentrations.[2] In the radiation-doped unquenched specimens, despite their lower injected resistivity, the amount of resistivity recovered in this interval was 10–15% greater than in the untreated specimens. The ratio of deuteron doses through the radiation-doped and untreated specimens is not known, but we believe that these doses differed by less than 10% in test irradiations 6 and 10.

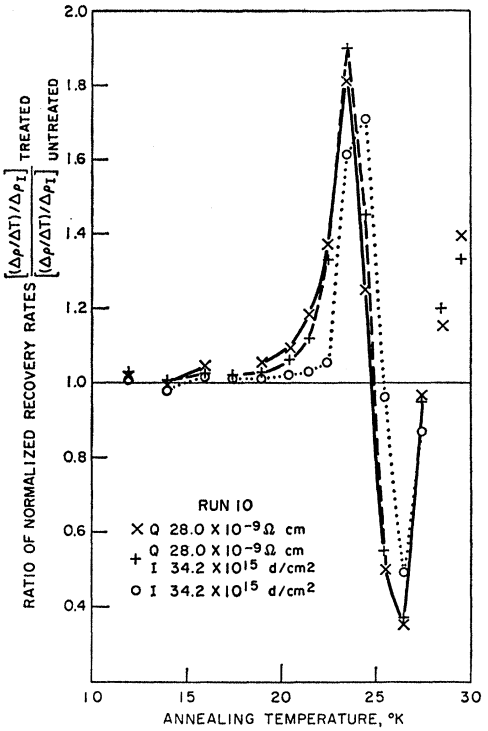

FIG. 6. Ratio of stage-I recovery rates for the specimens of test irradiation No. 10.

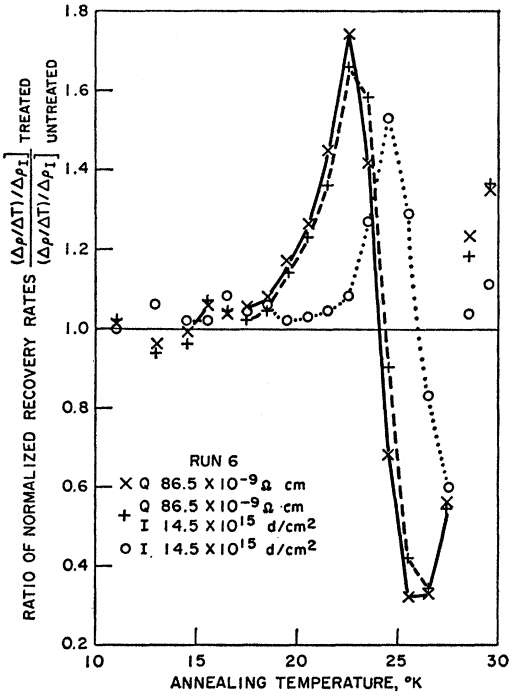

FIG. 5. Ratio of stage-I recovery rates for the specimens of test irradiation No. 6.

C. Recovery to 300°K

The annealing rate in all specimens is quite small through stage II, 35–240°K. About $\frac{1}{8}$ of the resistivity increment in an untreated specimen is recovered in this range. The annealing rate decreases to a minimum near 200°K. The only interruption to the decrease is a small recovery substage near 110°K.[2] The annealing rate becomes much larger again in stage III, which begins near 240°K and continues to above 300°K. The amount of recovery in that part of stage III studied in this investigation is about equal to the total recovery in stage II.

The effects of the different treatments given in platinum specimens before irradiation are emphasized in the plots of Fig. 7. To construct this figure, the per-

[24] T. H. Blewitt, R. R. Coltman, C. E. Klabunde, J. K. Redman, and J. Diehl, Bull. Am. Phys. Soc. 4, 135 (1959).

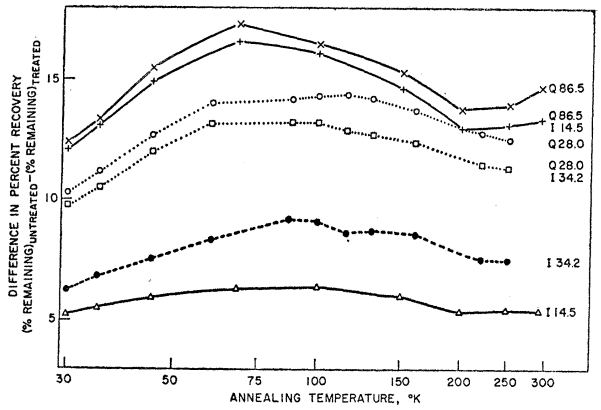

FIG. 7. Difference in percent of total damage recovered between treated and untreated specimens during stage II and the early part of stage III.

centage of resistivity increment remaining in the treated specimens after each annealing step is subtracted from the percentage remaining in the untreated specimen of that irradiation.[15] This suppresses the common background and reduces the effects of fluctuations in duration or temperature of the annealing pulses. These data show that radiation doping causes very little change in the fraction of resistivity that recovers between 30 and 300°K in untreated and in quenched platinum. All of the treatments increase the fraction of stage-II recovery that takes place below 100°K and reduce the fraction above that temperature. The magnitude of this shift increases with increasing resistivity injected by the preirradiation treatment. Quenched-in vacancies increase the amount of recovery in stage III,[2] but the limited data available here indicate that radiation doping does not increase recovery between 240°K and room temperature.

The specimen holder used in this work cannot be heated much above room temperature, so that we have no data on the recovery of the remaining damage. In an earlier report,[2] we showed that the remaining resistivity injected by quenching and by irradiation recovers in stage IV, 400–750°K. The deuteron fluxes through the specimens investigated in that work were larger than the flux of doping irradiation 6I and smaller than that of 10I.

IV. DISCUSSION

A. Mechanisms for Enhanced Resistivity Increments in Quenched Platinum

The initial rate of resistivity increase during low-temperature irradiation in many metals is increased by the preirradiation treatments, plastic deformation, the addition of substitutional impurities, and quenching.[7,8,24,25] Some workers have claimed that this extra resistivity represents deviations from Mattheissen's rule rather than the production of extra Frenkel pairs.[26] These deviations arise from anisotropic scattering at the defects introduced by the treatments, with the result that the increase in resistivity from the first Frenkel pairs produced in a treated specimen is greater than that of Frenkel pairs produced later in the irradiation of the treated specimen or at any time in an untreated one.

In a previous paper, we have given reasons for believing that the extra resistivity injected into treated specimens does represent, in large measure, extra point defects.[27] The case for our interpretation is particularly strong in the present instance of the extra-resistivity increment in quenched platinum. It is an essential consequence of the arguments based on deviations from Mattheissen's rule that the recovery of radiation-injected resistivity in treated specimens is enhanced only at the end of the recovery process. On the contrary, all of the extra resistivity in quenched platinum recovers well before the end of stage I. There remains a resistivity increment greater than half of that injected into untreated platinum by the same dose. It might be postulated that only the Frenkel pairs that recover by correlated recombination produce the deviations from Matthiessen's rule and not the more widely spaced pairs that recover above 23°K; but this argument is untenable, since the enhanced recovery always begins at 19°K, regardless of the ratio of the resistivity increment from irradiation to that from quenching or of the absolute value of either. It is also unreasonable to postulate that the scattering mechanism of the most widely separated Frenkel pairs that recover by correlated recombination is very greatly different from that of the pairs that recover by random migration.

The cross section for displacement to an interstitial site of an atom adjacent to a vacancy is increased over that for a normal atom by a factor considerably less than 2 for irradiation of platinum with 20-MeV deuterons. Thus displacements of the less tightly bound atoms adjacent to vacancies that would not have taken place in the absence of these vacancies increase the ratio of defect production rates in quenched-to-unquenched specimens by less than $12V_0$, where V_0 is the concentration of vacancies injected by the quench. Since initial increases of at least 20% are observed in the ratio of production rates for $V_0 \sim 10^{-4}$, these direct displacements do not contribute significantly to enhancement. Indeed, they could not be significant, or the defect production rate would increase with dose.

Since easier direct displacements at vacant sites are insufficient to explain the observed enhancements of production, a mechanism must be invoked which permits displacement events to sample much more of the lattice than the immediate surroundings of the initial displacement. This increases the probability of interaction with quenched-in defects. One method is

[25] M. L. Swanson, Phys. Status Solidi 23, 649 (1967).

[26] K. H. Fischer, Z. Kund. Mat. 6, 171 (1967).

[27] J. J. Jackson and K. Herschbach, Phys. Rev. 170, 618 (1968).

through replacement collision sequences which undergo directed defocusing at vacancy-type defects. In an earlier paper[2] we showed that there is evidence to support such a mechanism and in Sec. IV B we give further evidence that these sequences are responsible for much of the enhanced production in quenched platinum irradiated by 20-MeV deuterons.

Production of secondary displaced atoms can be enhanced at quenched-in defects by processes other than directed defocusing of sequences. Platinum atoms can receive up to 0.8 MeV from 20-MeV deuterons, and the average energy $\bar{E}_p$ given to primary displaced atoms in these irradiations is 370 eV. This is large enough so that most primary displaced atoms are able to displace several additional atoms. Such displacement cascades are frequently produced in irradiations with energetic particles of atomic size, but do not occur during irradiations with low-energy electrons. The maximum energy transferred to lattice atoms during the electron irradiations of platinum by Bauer and Goeppinger[23] was 65 eV. The average number $\bar{n}$ of displaced atoms per primary atom is approximately

$$\bar{n}=\bar{E}_p/2E_D \tag{4}$$

when $\bar{E}_p \gg E_D$, the threshold energy for displacement. In platinum, this latter energy is 36 eV,[28] so that $\bar{n}\sim 5$.

If at a set of sites the energy necessary to displace an atom permanently is reduced by Δ_i and the concentration of these sites is f_i, then the ratio of the number of secondary displacements in a lattice containing such sites to that in a lattice without these sites is

$$R=1+\sum_i \frac{f_i\Delta_i}{E_D-\Delta_i}. \tag{5}$$

The enhancement shown by Eq. (5) resembles the expression for enhancement of production of primaries at weak spots referred to above; but the enhancement of secondaries is larger, since

$$\bar{E}_s-E_D<\bar{E}_p-E_D. \tag{6}$$

In this expression, $\bar{E}_s$ is the average energy given to secondaries. Since a greater proportion of secondaries than primaries is produced with energies near the displacement threshold, the former are more sensitive to changes in this threshold. However, Eq. (5) shows that to give the enhancements observed for quenched-in vacancy concentrations of 10^{-4}, $\sum f_i\sim 10^3$ at each vacancy for sites at which $\Delta_i\sim\frac{1}{2}E_D$, or if only nearest neighbors to vacancies are significant, then $\Delta/(E_D-\Delta)\sim 100$. Such values are unreasonably high, so that it is not likely that this effect contributes more than 10% to enhancement.

When platinum is irradiated with electrons such that the maximum energy transferred to lattice atoms is less than $2E_D$, the enhancement of recovery below 23°K in quenched specimens is much less than the enhancement in similar specimens irradiated with 20-MeV deuterons.[23] This is further evidence that deviations from Matthiessen's rule are not a reason for the increased resistivity increment during irradiation and increased recovery during anneal of quenched platinum. This observation also limits the mechanisms of enhanced production to those which invoke the propagation of the effect of primary displacements through extended portions of the lattice. These long-range effects are much smaller in electron than in deuteron irradiations. Recovery above stage I is, to a large degree, a measure of the relative importance of long-range displacements. The fraction of damage that recovered above stage I in the work of Bauer and Goeppinger[23] is less than $\frac{1}{4}$ of that recovered in our untreated specimens given identical doses. Moreover, measurements indicate that, following electron irradiation, many of the defects that recover in stages II and III were produced initially as defects mobile in stage I which are trapped[29] or converted[30] during free migration in stage I, while most defects that do not recover in stage I after deuteron irradiation of platinum were directly created as defects first mobile in stages II or III.

B. Comparison of Effects of Radiation Doping and Quenching on Defect Production and Correlated Close-Pair Recovery

The quenching and radiation doping done in this work produce isolated and clustered point defects but do not appreciably change the dislocation density from that in well-annealed platinum. Since the enhanced resistivity produced in quenched platinum is associated with enhanced recovery in the range 19–23°K, the two effects will be considered together in this comparison of quenched-in vacancies with the defects remaining after radiation dopings. This identification of enhanced defect production with enhancement of a particular recovery process helps detect small changes in production. The difference in absolute resistivity increment between two specimens cannot be determined to better than 5%, but by means of the ratio plots described above, differences in recovery of 0.5% of total increment in an annealing pulse are easily seen.

Both treatments inject vacancies, but those from quenching enhance Frenkel-pair production and those from radiation doping do not. In the quenched specimens, a concentration of vacancies greater than that retained by the quench is present in equilibrium at the quench temperature, and, during the quench, these vacancies are both mobile and supersaturated. The

[28] W. Bauer and W. F. Goeppinger, Phys. Rev. 154, 584 (1967).

[29] C. L. Snead, Jr., Brookhaven National Laboratory Report No. BNL 50083, 1967 (unpublished).

[30] W. Bauer, A. Seeger, and A. Sosin, Phys. Letters 24A, 195 (1967).

vacancies injected by irradiation are produced singly and are never mobile before the test irradiation.

The free energy of a lattice supersaturated with vacancies is reduced if some of the vacancies associate to form vacancy pairs and perhaps larger clusters. During the quench, vacancies and divacancies remain in equilibrium with each other until a temperature T^* is reached below which the vacancies are not mobile enough to maintain equilibrium. Doyama[31] has derived an expression for T^* in terms of the other parameters of the quench. His analysis shows that T^* is decreased by increasing the concentration of vacant lattice sites present when the temperature nears T^* and by decreasing the cooling rate in this range. This means that the exponential cooling rates of the quenches in this work which retain many vacancies by their speed at high temperatures and allow many vacancy encounters to take place at temperatures where the divacancy binding energy is large compared with the thermal energy are particularly favorable for divacancy formation. For the quenched specimens described in this paper, $600<T^*<625$°K. At T^*, the ratio of single to divacancies is given by

$$C_{2v}/C_{1v}=6C_{1v}\exp(B/kT^*), \tag{7}$$

with the condition that

$$C_{1v}+2C_{2v}=C_T. \tag{8}$$

B is the divacancy binding energy. This binding energy is not well known for any metal. A value of 0.4 eV for B does not conflict with recovery data for platinum, but values 50% larger or smaller cannot be excluded. Computing C_T from a resistivity increment of 4×10^{-6} Ω cm/(at.% vacant sites), and using $B=0.4$ eV in Eqs. (7) and (8), the divacancy concentrations present at T^* in the largest quenches of irradiations 6 and 10 are 6.5×10^{-5} and 1.7×10^{-5}. The divacancy concentration increases below T^*, so that the final values are somewhat greater. Vacancy clusters that are larger than divacancies and stable at recovery temperatures are not formed by quenching pure platinum.[16]

After the doping irradiations and anneals at room temperature, the defects remaining in previously annealed specimens are vacancies and a somewhat smaller number of interstitials. The latter are grouped into clusters of at least two atoms. The annealing treatment is sufficient to remove all single interstitials, but the critical size n' of a cluster stable at room temperature is not known. Neglecting loss of interstitials to sinks other than vacancies, and taking the average resistivity of a vacancy plus an interstitial after the room-temperature anneal to be the same as the average resistivity of Frenkel pairs injected by electron irradiation at 4.2°K, 6×10^{-6} Ω cm/(at.%) [28]; then C_T before test irradiation 6 was 3.8×10^{-5} and before 10 was 8×10^{-5} in the annealed, radiation-doped specimens.

Since these vacancies are never mobile before the test irradiation (the mean time for a vacancy in platinum to make one change of position is several years at room temperature), the only divacancies present before the test irradiations are those created by displacements of atoms from adjacent sites. Double displacements from adjacent sites by one deuteron are exceedingly rare, and most divacancies result from successive displacements for which

$$C_{2v}=\int_0^{C_T}12P(1-c)cdc=6PC_T^2-4PC_T^3. \tag{9}$$

As mentioned above, the ratio of the cross sections for displacement of atoms adjacent to vacancies and of atoms in an undisturbed lattice, P, is limited to $1<P\ll2$, so that reasonable values for divacancy concentrations from Eq. (9) are $C_{2v}=1.3\times10^{-8}$, doping irradiation 6, and $C_{2v}=5.6\times10^{-8}$, doping irradiation 10. These are negligible combined with the concentrations resulting from quenches that give comparable values of C_T.

In an earlier paper, we suggested that the enhancement of defect production in quenched platinum takes place at divacancies.[2] That suggestion was based on the observation that after quenches from low temperatures, enhancement was negligible, and that the magnitude of enhancement increased more rapidly than linearly with C_T. The present observation that there is no enhancement in irradiation-doped specimens with comparatively large values of C_T but very small C_{2v} lends strong support to the divacancy model.

There remain to be considered the interstitial clusters from the radiation doping. If all interstitials are in clusters of two, then the concentration of these clusters is less than $\frac{1}{2}C_T$ or 1.9×10^{-5} in run 6 and 4×10^{-5} in run 10. (A small number of interstitials are lost to sinks other than vacancies, so that the number of interstitials in clusters is, in general, slightly less than the number of vacant lattice sites.) The data in Fig. 2 show that enhancements are observed in quenched specimens irradiated to give equivalent interstitial concentrations, so that the total absence of enhancement in annealed, radiation-doped specimens does not result from these clusters. Rather, it must result from the absence of sites, divacancies, at which enhancement takes place. However, these clusters increase disorder in the lattice. This blocks collision sequences resulting from displacements and reduces the number of such events that reach and interact with special lattice sites (dislocations and impurities) where reactions leading to enhanced production can take place.[27] The extra defects so produced are interstitials first mobile in stage III and their associated vacancies. The decrease in the number of these produced in radiation-doped specimens contributes to the small increase in the fraction of

[31] 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. 176.

total recovery that occurs in stage I below 23°K in such specimens as compared with untreated platinum. This is another manifestation of radiation annealing. The defects remaining from the radiation doping are less effective per vacancy-interstitial pair in damping the extra production than are the defects injected during irradiations near 4°K. Clustering of interstitials at room temperature reduces the total amount of lattice strain.

These conclusions are reinforced by our data on quenched then radiation-doped specimens. In these (irradiation 6, No. 3, and irradiation 10, No. 6), despite an increase in the number of vacant lattice sites after the radiation doping, the increase in resistivity during the subsequent test irradiation and the amount of recovery between 19 and 23°K are both less than in undoped, but otherwise identical, quenched specimens. During radiation doping, the concentration of divacancies is increased when new stable vacancies are created adjacent to quenched-in single vacancies and is reduced when interstitials are created near to and annihilate with one member of existing divacancies. The ratio C_{2v}/C_{1v} before irradiation is about $\frac{5}{6}$ for the largest quench of run 6 and 3/7 for the largest of run 10. Recovery data show that, for small doses and large quenched-in resistivities, the process by which divacancies are destroyed is favored over that by which they are created because of the enhanced defect production near divacancies,[2] but for the doses of doping irradiations 6I and 10I, the changes in divacancy concentration could not be detected. We believe that these changes are negligible for irradiation 6I and subsequent anneal and that a slight increase in divacancy concentration resulted from 10I. However, quenched specimens have a greater radiation-annealing effect then do unquenched specimens, and the interstitial clusters remaining from the doping irradiations reduce the number of interactions that produce extra defects at divacancies.

C. Defects from Quenching and from Radiation Doping as Sinks for Interstitials

In the region of stage-I recovery above 23°K, characterized by the random migration of interstitials to vacancy sinks, the defects injected by both treatments act the same. Both serve to increase the sink density. This is shown by the shape of the ratio plots in this interval. Recovery at the beginning is faster in the treated specimens because the mean separation between interstitials and vacancies is smaller; later, the rate in the treated specimens falls behind that in the untreated, since the number of reactants remaining is smaller in the former.

These extra sinks for interstitials can either be produced directly by the treatments and thus be present before the test irradiations or can be produced during the test irradiation as a result of greater Frenkel-pair production in the treated specimens. The latter possibility cannot explain our results. Measurements of the effect of dose on recovery[27] show that the resistivity recovered in the treated specimens must be more than an order of magnitude greater than in untreated ones to produce the deviations from unity in the ratio of recovery rates plotted in Figs. 5 and 6. The resistivity recovered between 23 and 28°K is the same in quenched as in untreated specimens, and is greater by less than 2% of total increment in the radiation-doped specimens than in the undoped ones.

Thus recovery during the first temperature interval in which interstitials sample a representative part of the lattice shows that both quenching and radiation doping inject defects that act as sinks for interstitials. Neither the degree of vacancy agglomeration nor the presence of immobile interstitial-type defects has much effect on recovery in this substage.

In principle, vacancies injected into a lattice before irradiation should also furnish additional sinks for correlated close-pair recombination. This is usually difficult to resolve from background recovery. One exception is the effect due to divacancies in quenched platinum. Then the extra interstitials are specifically produced close to divacancies, and a study of recovery in specimens quenched from high temperature and given smaller doses than in the present work shows that divacancies are destroyed preferentially during the annealing of these interstitials.[2]

Aside from this process, preexisting vacancies become sinks for correlated recovery of new interstitials only in a statistical way and at the expense of more distant pairs. These vacancies increase the probability that an interstitial produced in a second irradiation will be so close to a vacancy that the pair will combine rather than separate upon heating. If the number of such sites per vacancy is $M(C_T)$, then the ratio of close pairs in a specimen containing an initial concentration C_T of vacancies to those in a specimen initially free from vacancies is $R=1+M(C_T)C_T(1-f)/f$, where f is the fraction of Frenkel pairs that anneal by correlated recovery in an untreated specimen.

In platinum irradiated by 20-MeV deuterons, $f=\frac{1}{2}$ and the sites comprising $M(C_T)$ are about 100 in number, neglecting vacancy clustering and taking the third to seventh nearest-neighbor positions as close-pair sites. This is reduced by clustering, since the sites overlap. In the specimen quenched from the highest temperature, R is less than 1.02 and this effect cannot be distinguished from the much greater enhancement of production at divacancies. In the radiation-doped specimens of run 10, $1.005<R<1.008$, and this effect probably contributes somewhat less to enhancement of the fractional recovery rate in the close-pair region than does the reduction of conversion to stage-III interstitials discussed above.

D. Effects in Stage II

The effects of the defects from both treatments are similar in stage II. None of the treatments has much

effect on the fraction of damage that recovers in stage II, but all of them increase the amount of recovery between 35 and 100°K at the expense of recovery between 100 and 240°K. In an earlier paper,[2] we concluded that most of the recovery in stage II can well be explained on the basis of escape of mobile interstitials from traps; that the number of traps, which are mainly impurities, is unaffected by the presence of excess vacancies; and that the proximity of a vacancy reduces the activation energy for escape, with subsequent annihilation of the trapped vacancy. The present data fit this picture, with the vacancies from radiation doping serving the same rate as do the vacancies from quenching. Interstitial clusters have little effect on stage-II recovery. The magnitude of recovery is not changed by radiation doping nor does this treatment produce any annealing peaks in stage II not present in untreated platinum, so that these clusters do not trap crowdions.

E. Radiation Annealing

On the basis of the spontaneous-recombination models[4–6] mentioned in the Introduction, the defects introduced by both treatments of this paper should reduce the Frenkel-pair production rates in subsequent irradiations. From Eq. (3), if the ratio of the number of displaced atoms per incident deuteron is the same in quenched as in unquenched platinum, the ratio of the production rates in the specimen with the largest quenched-in vacancy concentration to that in an annealed specimen should be $(1-2\times10^{-4}v)$, where v is the spontaneous-recombination volume for an interstitial around a vacancy.

Within the dose range of the present work, the production rates in the quenched specimens are always greater than in annealed ones. For sufficiently large doses, however, enhanced production in quenched platinum by directed defocusing at divacancies should become negligible. Strains around interstitials injected by the irradiation would disturb lattice regularity to block almost all collision frequencies from reaching divacancies. Calculations by Cotterill and Doyama[32] show that relaxation around a split interstitial is at least double that around a vacancy, so that radiation-injected defects should be especially efficient in defocusing. Our observations show that above an injected resistivity of 60×10^{-9} Ω cm, the difference in the production rates between quenched and unquenched platinum does not change much. We take this resistivity to correspond to the Frenkel-pair concentration that effectively blocks collision-sequence–divacancy interactions.

We have irradiated three pairs of specimens, in which one member had a quenched-in vacancy concentration of about 2×10^{-4} and the other was well annealed, to resistivity increments greater than 60×10^{-9} Ω cm. For equal injected resistivities, the defect production rates above this resistivity were in the ratios

$$\text{quenched/not quenched} = 0.99,\ 1.01,\ \text{and}\ 1.04.$$

In Sec. IV A we showed that secondary displacements at quenched-in defects can contribute at most a few percent to production in these irradiations, so that our data show that

$$v < (1\pm\tfrac{1}{2})\times10^{2}\ \text{atomic sites}. \qquad (10)$$

The values of v from Eq. (10) are upper limits. There is no direct evidence from injection of extra vacancies that nonthermal recombination makes any contribution to radiation annealing.

The initial defect production rate in a specimen doped with both interstitial clusters of size n' and excess vacancies of concentration V_0 would, on the basis of spontaneous recombination, be reduced from the rate in a well-annealed specimen by the factor $[1-vV_0(1+\alpha/n')]$. There is evidence that v is the same for new vacancies that combine with preexisting interstitials as it is for new interstitials with old vacancies.[4] The factor α is the ratio of the recombination volume of a cluster of n' interstitials to that of a single interstitial. It should be slightly greater than unity. Taking $n'=2$, $\alpha=1.1$, and the value for V_0 calculated in Sec. IV B for the radiation doping of run 10, the ratio of production rates from this effect is $(1-12.4\times10^{-5}v)$. The observed value is 0.93 ± 0.025. This gives

$$v > (6\pm2)\times10^{2}\ \text{atomic sites}. \qquad (11)$$

The parameters used in Eq. (11) are chosen to minimize v. Since possible enhancement of production in the radiation-doped specimens by secondary displacements at vacancies was neglected, the value of v needed may be substantially larger than the above value.

The contradictory results of Eqs. (10) and (11) show that nonthermal recombination is not a sufficient explanation for the production-rate changes following treatments. The reductions due to such recombinations should remain a nearly constant fraction of the number of displacements regardless of dose. Since this is not true at the beginning of the irradiation, nonthermal recombination is eliminated as an important factor in the reduced production rate in the radiation-doped specimens. The value of v deduced from high-dose measurements in quenched specimens is substantially less than values that have been derived from extrapolations to saturation in other fcc metals.[33] We believe that the recombination models that Eq. (2) and analogous expressions are based upon[4–6,34] are

[32] R. M. J. Cotterill and M. Doyama, in *Lattice Defects and Their Interactions*, edited by R. R. Hasiguti (Gordon and Breach, Science Publishers, Inc., New York, 1967), p. 79.

[33] A. Sosin and W. Bauer, in *Studies in Radiation Effects*, edited by G. J. Dienes (Gordon and Breach, Science Publishers, Inc., New York, to be published).

[34] K. Dettman, G. Leibfried, and R. Schroeder, Phys. Status Solidi 22, 423 (1967).

unrealistic, and that a proper model of radiation annealing must consider cooperative effects in the recovery of very large supersaturations of point defects. For very small doses, the production effects seen in the radiation-doped material can be readily explained on the basis of blocking collision sequences by interstitial clusters.

F. Possible Instance of an Effect due to Deviations from Matthiessen's Rule

Recovery in stage I above 23°K is characterized by the random migration of one form of interstitial (the crowdion) to vacancy sinks. Evidence for this was given in Sec. IV C. For the doses used in the present work, this recovery is substantially complete at 28°K. In other irradiations using very small doses effects suggestive of free interstitial migration have been seen up to 35°K.[2] The recovery rate in the low-dose specimens, which at 23°K fell behind that in higher-dose ones for the reasons discussed in Sec. IV C, overtakes the rate in the higher at a temperature near 27°K which depends on the magnitude and ratio of the doses, and remains ahead up to about 35°K. This temperature also corresponds to that set by Bauer and Goeppinger[25] as the end of stage I. In Table II, we give the fraction of total damage that recovers in the interval 28–35°K in untreated specimens and in specimens that have received a variety of different treatments. These values are to be contrasted with the 14% recovery between 23 and 28°K in untreated platinum.

The greater recovery in the treated specimens may be an example of enhanced resistivity of a small concentration of one type of defect, the crowdion, in a lattice containing a much greater concentration of another type of defect. These other defects are presumably divacancies in the quenched specimens, interstitial clusters in the doped ones, both of these in the quenched and doped ones, and dislocations in the deformed specimen. Single vacancies, trapped crowdions, and single split interstitials must be much less effective than the above defects in enhancing the resistivity of crowdions, since the amount of recovery in the untreated specimens, which contain only these, is less. One must further postulate that electron scattering is much different from trapped crowdions than from crowdions that can migrate freely.

The above picture is attractive, since the largest effect is seen in the specimens with extra dislocations, the defects whose scattering is least isotropic. It is also reasonable that a cluster of interstitials of greater than atomic extent in two dimensions should differ appreciably in scattering from single interstitials.

There are also several objections to the interpretation of these results on the basis of Matthiessen's-rule deviations. Those are the following: (1) It is not evident that scattering from divacancies should be both much different than from crowdions and less isotropic than interstitial clusters; (2) the effect due to dislocations should be greatest in the absence of other point defects, but it is decreased by an annealing treatment which removes the point defects injected by the deformation; and (3) the enhancements are an order of magnitude larger than predicted for this effect.

TABLE II. Effect of various treatments on recovery between 28 and 35°K.

Treatment	Specimen run and position	Recovery (%)
Quenched	6-1	3.2
	10-1	3.0
Radiation-doped	6-5	2.4
	10-3	2.8
Quenched and doped	6-3	3.2
	10-6	2.9
Deformed, 50% reduction in thickness	8-2	4.9
	13-3[a]	3.9
Untreated	6-4	2.0
	10-4	1.9
	8-6	2.0
	13-4	2.0

[a] Specimen annealed at 310°C after deformation.

The increase in annealing rate in this interval may also be explained by the mechanism considered in Sec. IV D, the acceleration of the release of crowdions from traps by the proximity of vacancies. All of the treatments considered, except deformation with subsequent aging, inject excess vacancies, and in an earlier publication we showed that dislocation strain fields can also give this effect.[27] The magnitude of the enhancement increases with the concentration of vacancies and dislocations injected before the irradiation. We believe that this mechanism is far more important than the effect of possible deviations from Matthiessen's rule. Very careful measurements of the change of a parameter other than resistivity in this range are needed to determine whether more or just "more resistive" defects are going to sinks in this temperature interval.

G. Increasing the Ratio of Vacancies to Divacancies

When a quenched specimen is irradiated and then annealed at a temperature sufficient to remove all interstitials but at which vacancies are immobile (if such a temperature exists), then the number of vacant lattice sites will not be less than before the irradiation. If any interstitials are lost to sinks other than vacancies, then the number of the latter will increase. The present results show that for large deuteron doses, interstitial clusters are produced which survive into the temperature range of vacancy migration. Also, as the dose increases the importance of defocusing at divacancies decreases and that of divacancy production by displacement from sites adjacent to existing vacancies increases. However, when small doses are given to platinum specimens containing large concentrations of

vacancies and divacancies, the large ratio of vacancy sinks to mobile interstitials precludes cluster formation, and recovery of the injected interstitials is essentially complete in stage III. Since these interstitials were preferentially produced near divacancies, a greater fraction of divacancies than of single vacancies is removed during subsequent annealing. In principle, by repeated cycles of irradiation and anneal, the ratio of divacancies to single vacancies can be reduced from somewhat more than $6C_{1v}\exp(B/kT^*)$ to approximately the ratio of the concentration of divacancies made in the last irradiation that survive the anneal to the concentration of quenched-in vacancies V_0. The concentration of divacancies made in an irradiation that injects a concentration C of Frenkel pairs into a lattice containing V_0 isolated vacancies is

$$C_{2v}=\int_0^C 12P[1-(V_0+c)][V_0+c]dc, \qquad (12)$$

which, to first order in C, becomes

$$C_{2v}=12PV_0C[1-V_0]. \qquad (13)$$

Of these divacancies, at least half are removed in an anneal through stage III. The rate of approach to this concentration is considered in the next paragraph.

On the basis of the present work, it appears that the concentration of interstitials produced which combine in stage I with a divacancy is proportional to the concentration of divacancies. Thus, if the initial divacancy concentration is C_{2v0} and the constant of proportionality is K, then after n irradiations that would inject a Frenkel-pair concentration C in a lattice without divacancies, followed by anneals to remove all interstitials, the concentration of divacancies would be reduced to

$$C_{2vn}=C_{2v0}(1-KC)^n. \qquad (14)$$

The results of Ref. 2 show that for large values of C_{2v0}, concentrations C at least as large as 3×10^{-5} can be injected with essentially complete recovery of interstitials in stage III. About $\frac{1}{4}$ of that concentration of interstitials injected into a specimen containing the largest quenched-in vacancy concentration considered in this work recover by correlated recombination with divacancies. If the value of the divacancy binding energy used in Sec. IV B, 0.4 eV, is correct, then the factor K in Eq. (14) becomes 4×10^3, and 18 irradiations to $C=3\times10^{-5}$ are required to reduce C_{2vn} to below $0.1C_{2v0}$. As B increases, K decreases but the minimum value of K, corresponding to $B=\infty$, is 2.6×10^3. The process of conversion of divacancies to single vacancies would be much more efficient if B were appreciably less than 0.4 eV. A reduction of 25% in B would reduce the number of cycles needed to diminish C_{2v} by an order of magnitude from 18 to 9.

The process described in this section should be an effective, although tedious, means of reducing the ratio of divacancies to single vacancies. On the basis of the concepts developed in this paper, the success of the conversion process can be measured at any stage by comparing either the defect production rate or the rate of recovery between 19 and 23°K in the test specimen with the rates in an untreated specimen.

V. SUMMARY

The principal results of this investigation are as follows:

(1) The defects injected by quenching and those injected by irradiation in stages I or II followed by an anneal into stage III both serve as sinks for interstitials mobile in stage I.

(2) Residual interstitials clusters do not affect recovery in stages I or II.

(3) Divacancies in concentrations of the order of 10^{-5} or greater enhance defect production during irradiation with 20-MeV deuterons but equivalent concentrations of single vacancies do not.

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