Point-Defect Studies in Platinum by Electron Irradiation at Low Temperatures. I. Defect Production*

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The electrical resistivity increase per unit electron flux (damage rate) of 99.999%-pure 0.0002-in.-thick platinum foils was measured as a function of incident electron energy from 1.3 to 2.1 MeV near 9°K. Reasonable agreement between the theoretical displacement cross section, calculated with a unit displacement probability, and experimental data is achieved with an effective threshold displacement energy of 36 eV and a Frenkel resistivity of 6×10^{-4} Ω cm per unit fractional concentration Frenkel pairs. The ratio of the damage rate of platinum to that of gold is nearly independent of the electron energy for 45 eV $<T_m<72$ eV and decreases rapidly to zero for $T_m<45$ eV, where T_m is the maximum energy imparted to a lattice atom by a bombarding electron. These results are interpreted to indicate that indirect displacement processes occur in both metals near threshold.

I. INTRODUCTION

A RELATIVELY small fraction of the total effort in radiation-damage studies in metals has been devoted to platinum. The only recent work using electron irradiation has been the recent damage-rate measurements of Burke *et al.*[1] and the stage-IV recovery measurements of Bauer and Sosin.[2] (Preliminary results of this work were presented last year.[3]) The damage rate measurements of Burke cover a higher energy range (1.8–3.0 MeV) than this work (1.3–2.1 MeV). The experimental results presented in this paper are in excellent agreement with Burke's results in the overlapped energy range. In the following paper we present results of detailed recovery studies in stage I after 2-MeV electron irradiation.

The structure of these two papers on platinum is intentionally closely analogous to a recent series of three papers on gold by Bauer and Sosin.[4] This is due to the fact that the atomic number and chemical behavior of the two materials are sufficiently similar to allow almost identical experimental procedure and that the aim of the experiments was identical: An understanding of the displacement process and identification of the recovery stages. However, the experimental results presented here for platinum, especially in the second paper, are strikingly different from those of gold.

In Sec. II of this paper, a description of the experimental technique is given. The data are presented in Sec. III and a comparison with the theoretical displacement cross section is given in Sec. IV. Finally, a discussion of the results is given in Sec. V.

II. EXPERIMENTAL METHODS

A. Specimen Preparation

The specimens were 0.0002-in.-thick platinum foils. The foils were prepared by rolling between tantalum foils 99.999% pure 0.002-in.-diam wire purchased from Sigmund Cohn after a thorough cleaning.[5] A long section of the foil was preannealed in nitrogen gas at 750°C for 2 h by resistive heating. The actual specimen was then prepared from this foil by spot-welding 0.002-in.-diam platinum wire as potential leads. After mounting the specimen on the holder[6] and the holder in the cryostat, the foil was reannealed at 750°C for 2 h in nitrogen gas by resistive heating. Typical residual resistivities of the foils were 10^{-8} Ω-cm based on a room-temperature resistivity of 10^{-5} Ω-cm. The residual resistivity of the foils is probably size limited since the residual resistivity of the starting material (0.002-in. diam. wire) was of the order of 5×10^{-9} Ω-cm.

B. Irradiation

The cryostat and instrumentation has been described elsewhere.[6] The experimental accuracy of the resistivity readings was $\pm2\times10^{-12}$ Ω-cm. The estimated error in the integrated electron flux is approximately 5%. The electron energy was determined by a double 60° magnet system calibrated at 1.65 MeV with the $Be^9(\gamma,n)Be^8$ reaction.

The temperature of the specimens was held below 9°K with electron current densities of 2.5μA/cm². Special care has to be exercised to hold the irradiation temperature below the first major recovery peak at about 10°K (see following paper).

III. EXPERIMENTAL RESULTS

In Fig. 1 we show the experimental results of the resistivity increase per unit electron flux $d\rho/d\phi$ as a function of T_m, the maximum energy imparted a lattice

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[1] E. A. Burke, C. M. Jimenez, and L. F. Lowe, Phys. Rev. **141**, 629 (1966).

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

[3] Walter Bauer, in *Lattice Defects and Their Interactions*, edited by R. R. Hasiguti (Gordon and Breach Science Publishers, Inc., New York, to be published).

[4] Walter Bauer and A. Sosin, Phys. Rev. **135**, A521 (1964); **136**, A255 (1964); and **136**, A474 (1964).

[5] K. Herschbach, Phys. Rev. **130**, 554 (1963).

[6] A. Sosin and H. H. Neeley, Rev. Sci. Instr. **32**, 922 (1961).

atom by the bombarding electron. The experimental points in Fig. 1 include a correction for energy degradation of the bombarding electrons in the specimen. The correction procedure is identical to that in Ref. 4. The correction for electron straggling is small (<5%).

In addition to our results the lower energy experimental results of Burke *et al.*[1] are shown in Fig. 1. The agreement between our data and Burke's data is excellent. At lower energies one notes that the damage rate curve has a "tail." The displacements which give rise to the resistivity increase in the tail region are probably of an indirect nature,[3,7] which will be discussed in Sec. V. The presence of the tail in the damage rate curve introduces considerable uncertainty into the extrapolation of the curve to zero damage production.[7] This means that a precise value of T_d, the threshold displacement energy, cannot be deduced from our data in a direct manner.

IV. COMPARISON OF EXPERIMENTAL DATA WITH DISPLACEMENT THEORY

The comparison of the experimental values of $d\rho/d\phi$ with the displacement theory is afforded through the relation

$$d\rho/d\phi=\rho_F\sigma_d, \tag{1}$$

where ρ_F is the Frenkel resistivity and σ_d the displacement cross section.

The calculation of σ_d for high atomic number elements

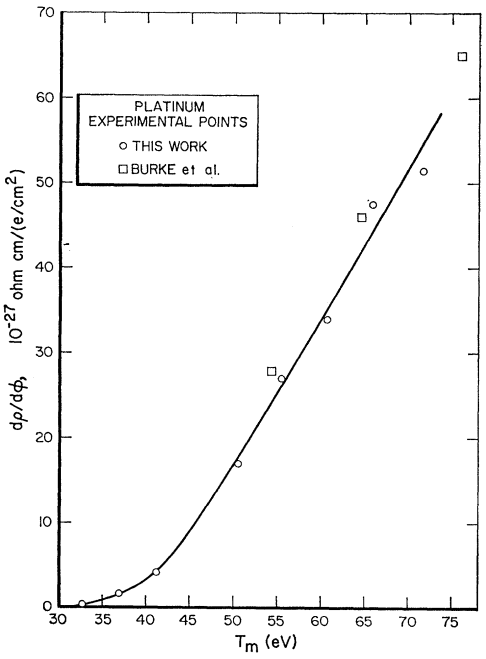

FIG. 1. The resistivity increase per unit electron flux $d\rho/d\phi$ as a function of T_m, the maximum energy imparted a lattice atom by an electron. The data of Burke *et al.* are from Ref. 1.

[7] Walter Bauer and A. Sosin, J. Appl. Phys. **37**, 1780 (1966).

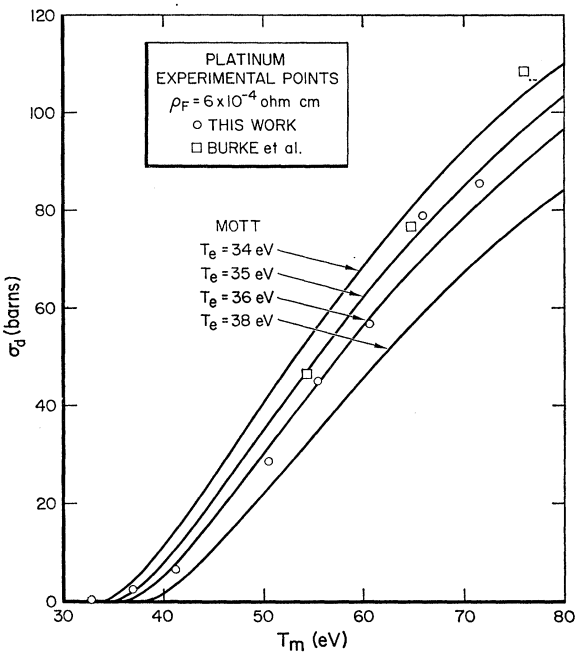

FIG. 2. The theoretical and experimental values of the displacement cross section σ_d as a function of T_m, the maximum energy imparted a lattice atom by an electron. The theoretical σ_d was calculated for T_e=34, 35, 36, and 38 eV. The experimental value of σ_d was determined from Eq. (1) and the indicated value of ρ_F.

proceeds as follows:

$$\sigma_d=2\pi\int_{\theta_m}^{\pi}\frac{d\sigma}{d\Omega}\sin\theta\,d\theta. \tag{2}$$

Here $d\sigma$ is the relativistic Coulomb scattering cross section due to Mott.[8] The minimum scattering angle of the incident electron θ_m is defined by

$$T_e=T_m\sin^2(\tfrac{1}{2}\theta_m), \tag{3}$$

where T_e is an effective threshold displacement energy. In this formulation it is implicitly assumed that the threshold displacement energy is essentially independent of the crystallographic direction into which the atom is driven as a result of the electron collision.

Numerical calculations of σ_d from Eq. (2) have been done by Khandelwal and Merzbacher,[9] Burke *et al.*,[10] and Oen.[11] The values of σ_d presented here in Fig. 2 were kindly made available to us by Khandelwal and Merzbacher. The "experimental" values of σ_d calculated, using Eq. (1) and a value of $\rho_F=6\times10^{-4}$ are also shown in Fig. 2. (Throughout this paper the units of ρ_F will be Ω-cm per unit fractional concentration Frenkel pairs.) Reasonably good agreement between

[8] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, New York, 1949), p. 78.

[9] G. S. Khandelwal and E. Merzbacher, Phys. Rev. **130**, 1822 (1963).

[10] E. A. Burke, N. Grossbard, and L. F. Lowe, Air Force Cambridge Research Laboratories Report No. AFCRL-65-286 (unpublished).

[11] O. S. Oen, Oak Ridge National Laboratory Report No. ORNL-3813, 1965 (unpublished).

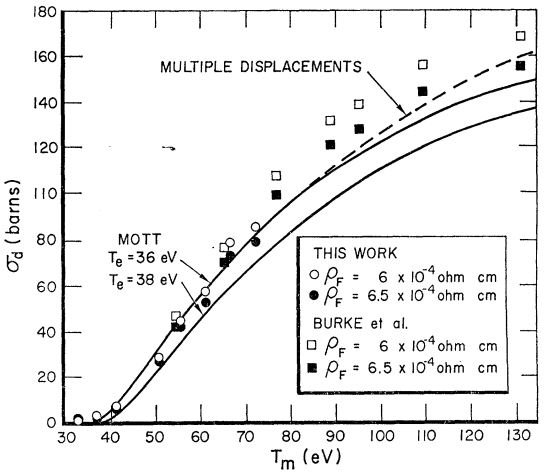

FIG. 3. The theoretical and experimental values of σ_d as a function of T_m. The theoretical value of σ_d was calculated for $T_e=36$ and 38 eV and the multiple displacement theory was from Ref. 1. The experimental value of σ_d was determined from Eq. (1) and the *two* indicated values of ρ_F.

theory and experiment is achieved for $T_e=36$ eV and $\rho_F=6\times10^{-4}$. In Fig. 3 we compare the experimental and theoretical values of σ_d to higher energies, using the results of Burke *et al.*[1] In order to demonstrate the sensitivity of the experimental value of σ_d to the choice of ρ_F we have plotted the results for $\rho_F=6\times10^{-4}$ and $\rho_F=6.5\times10^{-4}$. One notes that at higher energies a value of $\rho_F=6.5\times10^{-4}$ or even slightly larger is favored for $T_e=36$ eV. The data are also in reasonable agreement with the multiple-displacement theory chosen by Burke *et al.*[1]

An alternative method of comparing the experimental and theoretical values of σ_d involves normalizing the results at a particular energy. This approach allows one to choose a value of T_e for best agreement between theory and experiment without choosing a value of ρ_F. Many authors[1,4,12,13] have used this method with varying degrees of success. For example, in copper reasonable success has been achieved[12,13], whereas in gold this procedure was found to be inadequate.[4] In platinum Burke *et al.*[1] found for 55 eV $<T_m<$90 eV that the agreement between theory and experiment ($T_e=37$ eV, $\rho_F=7.5\times10^{-4}$) is approximately the same with either the normalization procedure (normalized at $T_m=54$ eV) or the method used in this work. They found that above $T_m=90$ eV the data are below the multiple displacement theory and at $T_m=130$ eV the data are less than the simple displacement theory. This is to be compared with the results shown in Fig. 3, where the data do not seem to fall below the theory ($T_e=36$ eV). An explanation for this discrepancy probably lies in the nature of the normalization comparison procedure. When the data and theory are normalized to a value of one at a particular energy one assumes, in effect, that there exists perfect agreement between theory and experiment at that energy. The relative difference between theory and experiment at other energies is then strongly dependent on the extent to which the data and theory actually agree at the normalization energy. This implies that the utility of the normalization procedure is dependent on the normalization energy (see for example, Ref. 4). Thus it may be that the normalization-comparison method in platinum yields only an apparent decrease in the data at higher energies.

V. DISCUSSION

Our experimental values of $d\rho/d\phi$ are in excellent agreement with the results of Burke *et al.* in the overlapped energy range. They found their data to be consistent with $T_e=37$ eV and $\rho_F=7.5\times10^{-4}$. These values are in reasonably good agreement with our values of $T_e=36$ eV and $\rho_F=6.0\times10^{-4}$. In fact, the actual agreement can probably be improved as is shown in Fig. 3. Therefore, one can conclude that the damage production in platinum, for 36 eV $<T_m<$130 eV, can be adequately described by a unit step displacement probability near $T_e=36-37$ eV and with $\rho_F=(6-7.5)\times10^{-4}$.

Recently Sherman *et al.*[14] studied the dependence of the theoretical value of σ_d in platinum on the choice of the probability of displacement function $P(T)$ (here assumed to be a unit step function at T_e). One of their conclusions particularly relevant to the present discussion is that σ_d is only weakly dependent on the choice of $P(T)$. Thus, to the extent that we assumed that there exists an energy T_e at which $P(T)=1$, the value of ρ_F deduced here should be relatively insensitive to the details of the displacement process.

We now turn to a discussion of the ρ_F value deduced here. There exists no independent measurements of ρ_F. One may get an estimate of ρ_F from the relation $\rho_F=\rho_i+\rho_v$, where ρ_i= resistivity of an interstitial, and ρ_v the resistivity of a vacancy. In platinum neither ρ_i nor ρ_v are known, whereas in some other metals at least an accurate value of ρ_v is available.[3] It has been pointed out by Lucasson and Walker[15] that ρ_F is approximately proportional to the normal resistivity at 0°C. Using this simple proportionality we deduce ρ_F values of platinum of 4.1, 7.6, and 12.5×10^{-4} based on the ρ_F and normal resistivity data of nickel, copper, and iron, respectively. [Here we used the ρ_F data of Lucasson and Walker[13] and the Handbook of Chemistry and Physics (Chemical Rubber Publishing Company) values of the normal resistivities of nickel, copper, and iron.] The value of ρ_F for platinum seems to agree with that deduced from the copper data quite well, and is within a factor of 2 of the ρ_F values deduced from nickel and iron.

[12] A. Sosin, Phys. Rev. **126**, 1698 (1962).
[13] P. G. Lucasson and R. M. Walker, Phys. Rev. **127**, 485 (1962).
[14] C. H. Sherman, L. F. Lowe, and E. A. Burke, Phys. Rev. **145**, 568 (1966).
[15] P. G. Lucasson and R. M. Walker, Phys. Rev. **127**, 1130 (1962).

Our value of T_e follows the qualitative prediction of Lucasson and Walker.[15] They pointed out that for closely related metals the threshold energy should increase with the ratio of Z^2/r_0, where Z is the atomic number and r_0 the lattice parameter. Using the value of $T_e=35$ eV for gold[4] we deduce $T_e=35.5$ eV for platinum. The semiempirical calculations of Anderson and Sigmund[16] using a Born-Mayer potential predict values of T_d of 50 and 51 eV in the (100) and (110) directions for platinum. These values are somewhat larger than our experiments indicate.

In the following paper we will discuss the resistivity recovery data of platinum after 2-MeV electron irradiation. These data lend themselves to an interpretation which is different from that given for the gold recovery data.[4] Thus it is desirable to investigate whether the displacement processes in platinum and gold are also fundamentally different. We first compare the $d\rho/d\phi$ data presented here for platinum with the data for gold in Fig. 1 of Ref. 4. The ratio of the damage rate in platinum to that in gold is plotted as a function of T_m in Fig. 4. The T_m values of gold and platinum are sufficiently similar for a given electron energy that the average value of T_m was used in Fig. 4. One notes that for $T_m>45$ eV the ratio is essentially constant (≈ 6) and for $T_m<45$ eV the ratio decreases to near zero at 33 eV. From Eq. (1) we have

$$\frac{(d\rho/d\phi)_{\mathrm{Pt}}}{(d\rho/d\phi)_{\mathrm{Au}}}=\frac{\rho_F{}^{\mathrm{Pt}}}{\rho_F{}^{\mathrm{Au}}}\cdot\frac{\sigma_d{}^{\mathrm{Pt}}}{\sigma_d{}^{\mathrm{Au}}}. \tag{4}$$

For metals with almost identical values of atomic number and weight, and identical T_e, we expect the ratio of the displacement cross sections to be nearly independent of T_m. Thus one would expect $(d\rho/d\phi)_{\mathrm{Pt}}/(d\rho/d\phi)_{\mathrm{Au}}$ to be independent of T_m if $T_e{}^{\mathrm{Pt}}\approx T_e{}^{\mathrm{Au}}$ and ρ_F is independent of T_m. This is indeed the case for 45 eV $<T_m<70$ eV.

In order to explain the decrease in the ratio of $(d\rho/d\phi)_{\mathrm{Pt}}/(d\rho/d\phi)_{\mathrm{Au}}$ for $T_m<45$ eV we have investigated the effect on σ_d of slightly different values of T_e

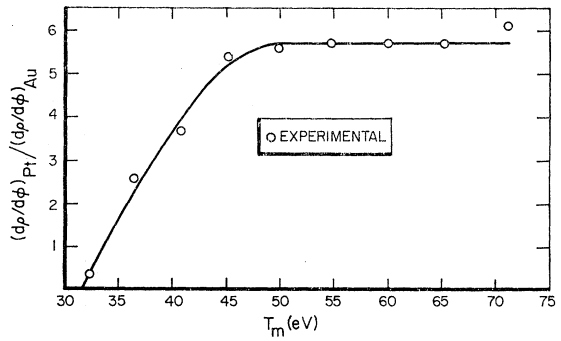

FIG. 4. The ratio of the damage rate of platinum (this work) to that of gold (Fig. 1, Ref. 4) as a function of T_m.

[16] H. H. Anderson and P. Sigmund, Danish Atomic Energy Commission Risö Report No. 103, 1965 (unpublished).

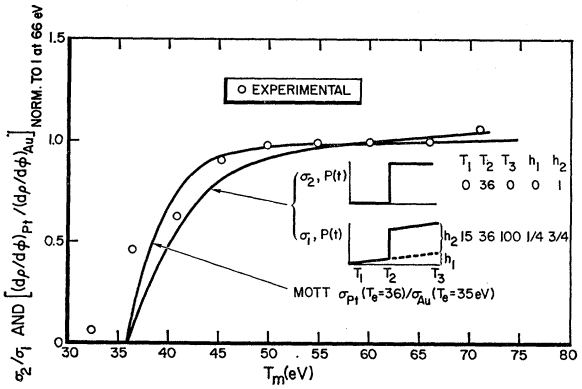

FIG. 5. The data of Fig. 4 replotted normalized to 1 at 60 eV. The ratio of theoretical displacement cross sections calculated as described in the text.

by calculating $\sigma_d{}^{\mathrm{Pt}}(T_e=36\text{ eV})/\sigma_d{}^{\mathrm{Au}}(T_e=35\text{ eV})$ and secondly incorporating indirect displacement processes[3,7] in the cross-section calculation for gold. The results of these calculations and the experimental results of Fig. 4 are shown in Fig. 5, normalized to unity at $T_m=60$ eV. One notes that $\sigma_{\mathrm{Pt}}(T_e=36)/\sigma_{\mathrm{Au}}(T_e=35)$ is a constant for $T_m>45$ eV, as expected, and then decreases to zero somewhat faster than the data. To achieve better agreement with the data would require unrealistically low values of $T_e{}^{\mathrm{Pt}}$ in the cross-section calculation. This indicates that different T_e values in gold and platinum can at best only be used to explain part of the decrease in the ratio of $(d\rho/d\phi)_{\mathrm{Pt}}/(d\rho/d\phi)_{\mathrm{Au}}$ at lower energies.

In order to incorporate indirect displacements into the cross section calculation we refer to the Seitz-Koehler[17] formulation:

$$\sigma_d=\int_{T_e}^{T_m}P(T)\frac{d\sigma(T)}{dT}dT, \tag{5}$$

where $P(T)$ is the probability of displacement function and $d\sigma(T)$ the differential energy transfer cross section. This formulation has been used extensively by Lucasson and Walker[13] for a variety of $P(T)$ functions. The reader is referred to Ref. 13 for a detailed discussion of Eq. (5). It should be noted that the calculation of σ_d by Eq. (5) for high-Z elements is a poor approximation. However, in this case we have only calculated the ratio of the cross sections of two very similar elements in which case the correction should be small. In Fig. 5 we plotted a simple step function $P(T)$ at $T_e=36$ eV, appropriate for platinum (σ_2), and a linear $P(T)$ function with a $\frac{3}{4}$ step at $T_e=36$ eV, appropriate for gold (σ_1). The linearly rising part of the gold $P(T)$ function is meant to represent indirect displacements. The plot of σ_2/σ_1 falls below the data at lower energies. It seems clear that better agreement may be obtained upon incorporating indirect displacements in the platinum cross-section

[17] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. II, p. 330.

calculation. It is very likely that a good fit between theory and experiment may be achieved with the use of an arbitrary choice of $P(T)$ functions. However, until the indirect displacement mechanism is understood in detail such mathematical exercises possess little physical significance. The important points are that the displacement probability in either metal gradually goes to zero below T_e and secondly that for, 45 eV $<T_m<70$ eV, the data are consistent with the theory based on nearly the same values of T_e.

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Point-Defect Studies in Platinum by Electron Irradiation at Low Temperatures. II. Resistivity Recovery from 10 to 300°K*

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Pairs of 99.999%-pure platinum wires were irradiated with equal doses below 10°K and annealed simultaneously. The recovery spectrum of both wires was closely identical. However, when one of the wires was quenched prior to the irradiation, the irradiation-damage recovery was remarkeably different from that of the unquenched wire: The ratio of the rate of recovery of the quenched to the unquenched wire was nearly 1 from 10 to 24°K, near 2 from 24 to 27°K, and near 0 from 28 to 32°K. The amount of recovery of the quenched sample was enhanced 7% over the unquenched sample. These results are strong evidence for long-range (uncorrelated) migration of an interstitial near 28°K. Only a few percent recovery takes place in either the quenched or the unquenched sample between 35 and 300°K. These observations, combined with other relevant experimental results and calculations based on chemical rate theory, provide evidence that the defects remaining above 35°K are mainly trapped interstitials, di-interstitials, and vacancies. Stage III is due to the release of trapped interstitials and the migration (or dissociation) of dimers. The vacancies migrate near 600°K (stage IV).

I. INTRODUCTION

IN the preceding paper[1] we presented experimental results related to the displacement cross section and threshold displacement energy in platinum using electron irradiation. In this paper we present the experimental recovery results in particular from 8 to 30°K (stage I) and related calculations based on chemical rate theory.

The recovery results of stage I presented here are the first after electron irradiation. Bauer and Sosin[2] studied the stage-IV (~600°K) recovery in platinum after electron irradiation near 80°K. They concluded that the stage-IV recovery is due to the diffusion of single vacancies to sinks with concurrent trapping by impurities. This result is incorporated in a recovery model presented here. Previously, the stage-I recovery has been studied after neutron irradiation by the Oak Ridge[3] and Munich[4] groups. They found a number of well-defined annealing peaks whose position in temperature is in good agreement with the results of the present work. The stage-I recovery of deuteron-irradiated platinum was studied by Herschbach and Jackson.[5] They also investigated the influence of prequenching on the irradiation damage recovery. Their results are in qualitative agreement with the results presented here.

The primary reason for undertaking a detailed study of the stage-I recovery after electron irradiation was to ascertain whether or not uncorrelated or random migration of the interstitial takes place near the end of the stage. The method used in this work closely parallels the pioneering work of the GE group[6] on copper, later work on gold by the Atomics International group[7] and

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[2] A. Sosin and Walter Bauer, Phys. Rev. **147**, 478 (1966); Walter Bauer and A. Sosin, *ibid.* **147**, 482 (1966).

[3] R. R. Coltman, C. E. Klabunda, K. L. McDonald, and T. K. Redman, J. Appl. Phys. **33**, 3509 (1962).

[4] G. Burger, K. Isebeck, J. Volkl, and H. Wenzl, J. Appl. Phys. **36**, 3356 (1965).

[5] J. J. Jackson and K. Herschbach, Bull. Am. Phys. Soc. **11**, 210 (1966); **10**, 1094 (1965).

[6] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. **114**, 1460 (1959).

[7] Walter Bauer and A. Sosin, Phys. Rev. **135**, A521 (1964).