

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 remarkably 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 paper¹ 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 Sosin² studied the stage-IV ($\sim 600^\circ\text{K}$) 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 Ridge³

and Munich⁴ 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 group⁶ on copper, later work on gold by the Atomics International group⁷ and

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).

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¹ Walter Bauer and W. F. Goepfingger, preceding paper, *Phys. Rev.* **154**, 584 (1967).

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

copper and aluminum by the Northwestern group.⁸ The type of measurements necessary to demonstrate random interstitial migration are based on the following principles: (1) Close Frenkel-pair recovery or correlated migration of the interstitial is independent of the concentration of vacancies since each interstitial is annihilated at the vacancy at which it originated. (2) If the interstitial migrates in an uncorrelated fashion, i.e., is no longer constrained to return to its vacancy, then the nature of the recovery (the recovery rate and under certain circumstances the amount) will depend on the concentration of vacancies. A concentration dependence of the recovery may also be observed under special circumstances without the uncorrelated or long range migration of the interstitial. This possibility is discussed in detail in Sec. VI of this paper.

We have introduced directly an excess vacancy concentration in one of the two platinum samples prior to the irradiation by quenching *in situ* from 1300°C to room temperature. In our experiments a pair of samples is irradiated and annealed simultaneously. The experimental method and results are given in the next two sections. The interpretation of the results is presented in Sec. IV. Calculations based on chemical rate theory and relevant experimental results are described in Sec. V.

In the last section we summarize our results and present a comprehensive recovery model for platinum based on additional experimental results. The applicability to the recovery of platinum of other recovery models previously evolved, primarily from a study of copper, are discussed.

II. EXPERIMENTAL METHODS

The experimental procedure was essentially the same as described in the previous paper.¹ In this case the specimens were 0.002-in.-diam wire which, after annealing and mounting had a residual resistivity of approximately $5 \times 10^{-9} \Omega \text{ cm}$.

The quenching *in situ* of one of a pair of specimens to room temperature was achieved by resistively heating in nitrogen gas and then turning the current off. This type of quench is roughly half as efficient as water quenching. After the quench, both specimens were cooled to near 4.2°K. and the irradiation initiated. All irradiations were conducted with 2-MeV electrons. This results in a maximum energy transfer of approximately 60 eV to a lattice atom. The temperature of the specimens during the irradiation was held below approximately 8°K.

Five-minute isochronal annealing pulses in relatively small temperature steps of 0.6°K (below 28°K) were taken in an attempt to resolve any "fine structure" of

stage I as found by the Northwestern group in copper⁹ and aluminum.¹⁰ Only four well-defined recovery peaks whose width at half maximum is approximately $T/10$, where T is the peak temperature, may be clearly identified between 10 and 30°K in platinum. A number of poorly defined "bumps" or shoulders are also present in the recovery spectrum. In contrast, some 20 or so peaks were found in copper⁹ and aluminum.¹⁰

III. EXPERIMENTAL RESULTS

A. Recovery

In this section we present the results of the irradiation damage recovery measurements of the same pair of samples with different pre-irradiation treatments. The relevant resistivity data such as residual resistivity ρ_0 , irradiation-induced resistivity increase $\Delta\rho$, and quenched-in resistivity ρ_q are summarized in Table I for some of the runs for which results are presented.

In Figs. 1 to 6 we present the experimental recovery measurements of runs I, II, and V. The important features to be observed are as follows:

1. Both the fractional recovery (Fig. 1) and the slope of the fractional recovery, (recovery rate), (Fig. 2) are closely identical of both *unquenched* samples in run I. There is an initial difference in the recovery because of slightly different irradiation temperatures of the two samples in a temperature region ($< 8^\circ\text{K}$) where some recovery takes place. This difference is of no significance in the interpretation and discussion presented in the following sections. In order to check this point we have irradiated the same pair of samples with a considerably smaller electron flux which results in lower and more nearly equal specimen temperatures. The low-temperature recovery of this carefully controlled irradiation is shown in Fig. 3. One notes that the recovery of both samples is essentially identical.

2. When *one* of the samples (B) is prequenched (run V) the amount of recovery above about 23°K is enhanced as seen in Fig. 4. There is also a pronounced difference in the recovery rate in the temperature range 23 to 33°K (Fig. 5). The prequenched sample recovery

TABLE I. Summary of resistivity data.

Run	$\rho_0 (10^{-9} \Omega \text{ cm})$		$\Delta\rho (10^{-9} \Omega \text{ cm})$		$\rho_q (10^{-9} \Omega \text{ cm})$		%Recovery at 37.4°K	
	A	B	A	B	A	B	A	B
I	4.1	5.2	2	2.4	0	0	91.3	91.6
II	4.1	4.7	2	2.5	12.7	0	96.8	90.2
V	5.8	5.0	1.7	1.7	0	23.3	92.0	97.9
VIII	5.9	5.0	0.2	0.2	0	23.3	89.3	95.9

⁸ G. W. Iseler, H. I. Dawson, and J. W. Kauffman, in *Lattice Defects and Their Interactions*, edited by R. R. Hasiguti (Gordon Breach Science Publishers, New York, to be published).

⁹ G. W. Iseler, H. I. Dawson, A. S. Mehner, and J. W. Kauffman, *Phys. Letters* **17**, 212 (1965).

¹⁰ H. I. Dawson, G. W. Iseler, A. S. Mehner, and J. W. Kauffman, *Phys. Letters* **18**, 247 (1965).

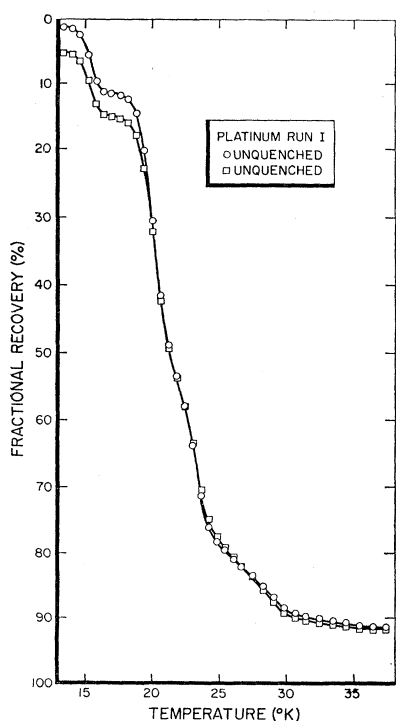


FIG. 1. The resistivity recovery as a function of annealing temperature in run I of a pair of specimens with identical pre-irradiation treatment. The specimens were annealed simultaneously.

rate is larger and there is a shift to lower temperature with respect to the unquenched sample.

3. Below 23°K the amount of recovery and re-

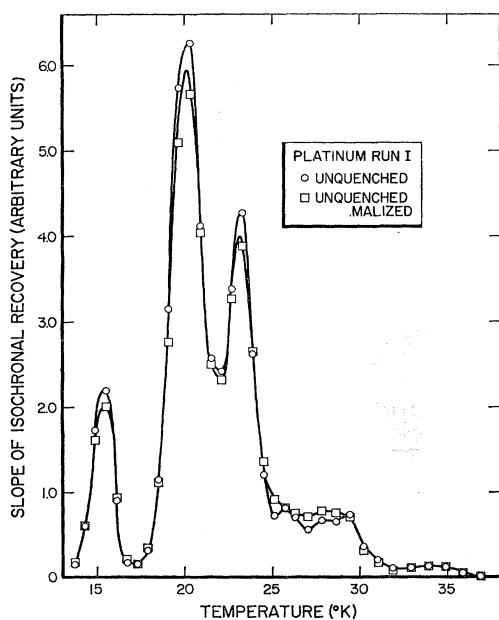


FIG. 2. The slope of the resistivity recovery as a function of temperature in run I of a pair of specimens with identical pre-irradiation treatment. The specimens were annealed simultaneously.

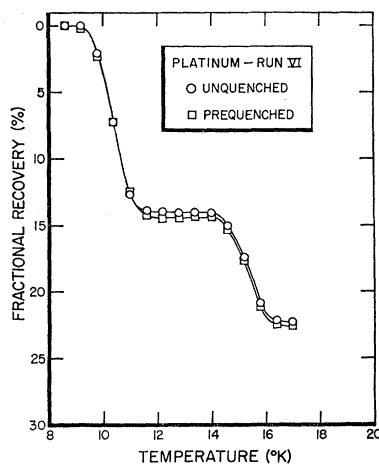


FIG. 3. The low-temperature resistivity recovery of a pair of specimens as a function of annealing temperature. Both specimens were irradiated at a lower temperature than the other runs for which data are presented here.

covery rate are relatively unaffected by the prequench treatment.

4. The results described in (2) and (3) above are reproduced when the quenching procedure is reversed (sample A is prequenched) as is seen in Fig. 6.

B. Activation Energy

We have analyzed the recovery in the temperature region of interest, 23 → 30°K, for the activation energy of motion by the Meehan-Brinkman¹¹ (MB) method. In addition to the isochronal recovery results already

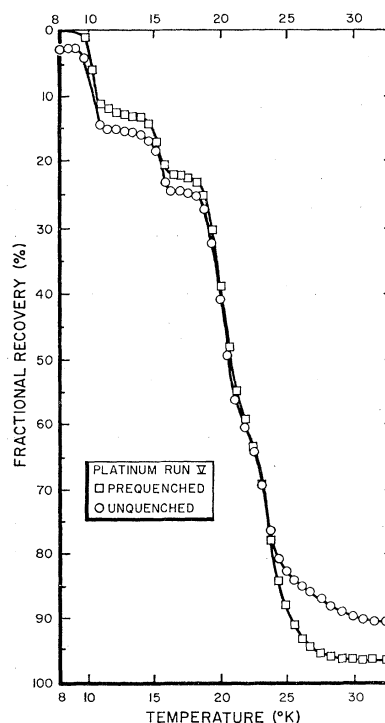


FIG. 4. The resistivity recovery as a function of annealing temperature in run V of a pair of specimens. One of the specimens was quenched prior to the irradiation. Both specimens were annealed simultaneously.

¹¹ C. J. Meehan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

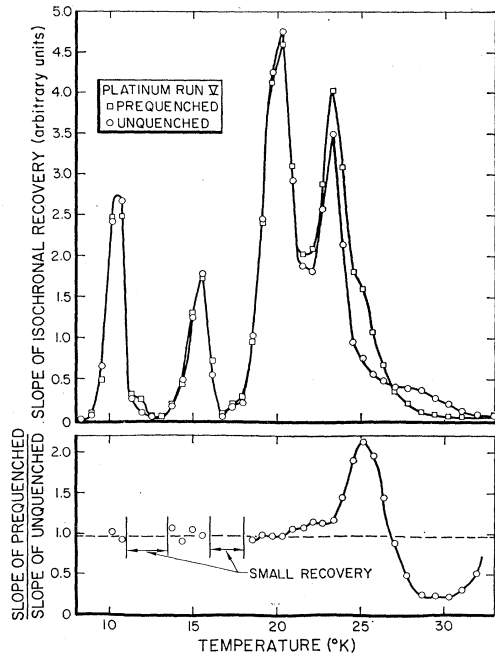


FIG. 5. Upper plot: The slope of the resistivity recovery as a function of temperature in run V of a pair of specimens. One of the specimens was quenched prior to the irradiation. Lower plot: Ratio of the recovery slope of the prequenched to the unquenched specimens as a function of temperature for run V.

shown isothermal recovery results are necessary for the application of the MB method. These isothermal results are shown in Fig. 7. We note that the irradiation damage recovery of the prequenched sample is different from the unquenched one and that the amount of recovery is larger.

The results of the MB method applied to the data of Figs. 7 and 4 are shown in Fig. 8. For an explanation of this method and the symbols used in Fig. 8, the reader is referred to Refs. 11 and 12. The recovery from approximately 24 to 27°K of both the prequenched and unquenched samples is uniquely activated with the same activation energy of 0.065 ± 0.005 eV. The fact that even the deviation of the data near 28°K from the straight line in Fig. 8 is the same for both samples is

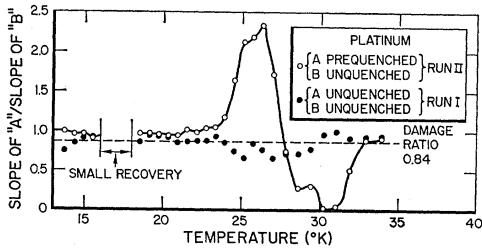


FIG. 6. Ratio of the recovery slope of the prequenched to the unquenched specimens of run II and of the two unquenched samples of run I as a function of temperature.

¹² Walter Bauer and A. Sosin, Phys. Rev. **136**, 474 (1964).

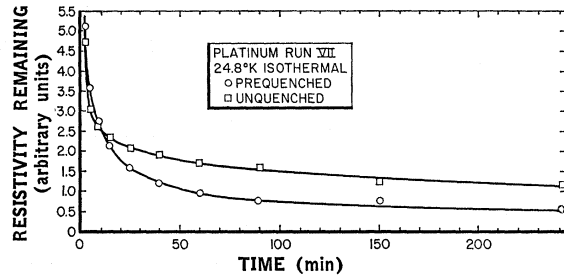


FIG. 7. The resistivity recovery as a function of time at 24.8°K of a pair of specimens annealed simultaneously. One of the specimens was quenched prior to the irradiation.

additional evidence that the same defect migrates in both samples.

IV. INTERPRETATION OF STAGE-I RESULTS

1. Since the recovery below about 23°K is unaffected by a relatively large excess vacancy concentration, the recovery is due to the recombination of Frenkel pairs in a correlated manner. That is, each interstitial returns to the vacancy from which it originated.

2. In the temperature range 23 to 30°K an excess vacancy concentration increases the amount of re-

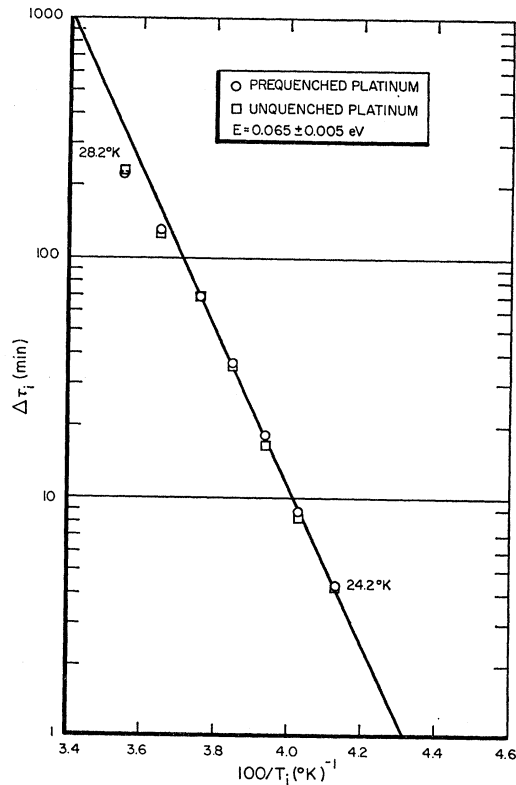


FIG. 8. The results of the Meechan-Brinkman activation energy analysis applied to the recovery data near 24.8°K. $\Delta\tau_i$ is the equivalent annealing time at 24.8°K (data of Fig. 7) and T_i is the temperature of the i th isochronal pulse (data of Fig. 4).

covery; correspondingly, the rate of recovery increases and is shifted to lower temperature. The *same* defect migrates in both the unquenched and prequenched samples. This provides strong evidence that the free or uncorrelated migration of the interstitial takes place near 28°K with an activation energy of 0.065 ± 0.005 eV.

3. A small fraction of the damage introduced near 4.2°K remains after anneal at 37.4°K, as can be seen in Table I. The question arises as to what defects are responsible for the fraction of damage remaining. There are at least three possibilities which have been discussed in the literature, mainly in connection with copper, but apply equally well here:

(a) Some of the migrating interstitials are trapped mainly at residual impurities and are only released at higher temperatures. The remaining defects after stage I are then the trapped interstitials and a corresponding number of vacancies.

(b) Some of the migrating interstitials interact with each other sufficiently to form an interstitial complex. We assume this complex to be a di-interstitial (dimer) which is mobile only at higher temperatures. The remaining defects are then the dimers and a corresponding number of vacancies.

(c) A second type of interstitial is produced by the irradiation which is *not* mobile near 28°K. The remaining defects are then the second type of interstitial and the corresponding number of vacancies.

We feel that, for the purity of samples used in the present experiments, impurity trapping is an important process. To this extent we will demonstrate in the next section by calculations based on chemical rate theory that an impurity trapping model can account semi-quantitatively for most of our results. Nevertheless evidence exists that some dimer formation may be taking place near 28°K.

We turn first to a discussion of the evidence for dimer formation. One of the predictions of this model is that the amount of recovery associated with annihilation and dimer formation is independent of the initial defect concentration for an unquenched sample in the absence of other reactions. The extent to which this prediction is borne out by the experimental results is seen in Table I, for sample A, runs V and VIII. We note that the recovery at 37.4°K of run VIII is approximately 3% less than run V in which there was considerably larger defect concentration. This 3% difference amounts to approximately 10% of the recovery between 23 and 34°K, which is a more appropriate measure of the uncorrelated recovery. This 10% difference is not consistent with dimer formation; on the other hand, while it is in the direction predicted by impurity trapping, the magnitude of the effect is smaller than predicted by the simple theory (see below). If dimer formation were dominant, the amount of recovery at 34°K in the prequenched sample would be expected to increase with

decreasing defect concentration (smaller $\Delta\rho$), contrary to the experimental results of runs V and VIII. A second prediction of the dimer model is that the concentration of defects remaining at 80°K, after irradiation at 4.2°K and annealing up to 80°K, is larger than the concentration of defects created after irradiation at 80°K to the same dose. This is due to the negligibly small instantaneous interstitial concentration in direct 80°K irradiation which inhibits dimer formation. Using the results of the preceding paper¹ and the damage rates of 80°K irradiations² we find that, indeed, the 8°K irradiations with subsequent warm up to 80°K resulted in approximately twice as much damage as the direct 80°K irradiations. This factor was observed to be near three for *zone-refined* copper by Corbett *et al.*⁶ Again the lesser relative purity of our platinum samples can qualitatively account for this difference since impurity trapping is insensitive to the interstitial concentration.

According to the third possibility (c), one interstitial is mobile near 28°K, and a second type of interstitial is mobile only at higher temperatures (stage III). An upper limit is placed on the percentage of the total damage consisting of the second type of interstitial (excluding close pairs) by the amount of recovery remaining at 37.4°K in the prequenched sample. This percentage can be evaluated from the results in Table I with the assumption that half the remaining damage consists of vacancies. Thus we conclude that at most 1 to 2% of the total resistivity increase consists of a second type of interstitial, *if* a second type of interstitial is created by 2-MeV electron irradiation at all.

We now turn to a discussion of several experimental results from the literature which indicate in varying degrees the importance of interstitial impurity interaction below or at 80°K. The first of these is a series of platinum irradiations near 80°K conducted for a study of the stage-IV recovery region ($\sim 600^\circ\text{K}$).² In that work it was concluded that single vacancies migrate in stage IV. However, in these experiments considerable recovery occurred also near room temperature (stage III). Since dimer formation at 80°K is negligible, we interpret these results to indicate that those interstitials created at 80°K which do not annihilate at vacancies are trapped at impurities and are subsequently released in stage III. Secondly, Neely and Sosin¹³ reported recently on some extended irradiations of copper and aluminum above stage I. They were able to fit their production data to a model of interstitial annihilation at vacancies and trapping of interstitials at impurities. Thirdly, well-established evidence¹⁴ has existed for some time demonstrating that the addition of small concentrations of selected impurities suppresses the recovery near the end of stage I in copper and aluminum.

¹³ H. H. Neely and A. Sosin, *Phys. Rev.* **149**, 535 (1966).

¹⁴ See for example, A. Sosin and H. H. Neely, *Phys. Rev.* **127**, 1465 (1962).

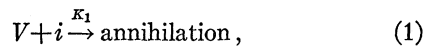
V. CHARACTERISTICS OF RECOVERY FROM 21–34°K

A. Theory

To get a more detailed understanding of the recovery process from 21 to 34°K, we consider the problem of *random* vacancy-interstitial annihilation with concurrent impurity-interstitial trapping.

After electron irradiation equal numbers of vacancies and interstitials are produced. Also, since the recovery up to 21°K is due to the annihilation of close Frenkel pairs, the numbers of vacancies and interstitials are equal at the beginning of free interstitial migration. Alternatively an excess vacancy concentration is assumed to be present in the lattice because of the quench of one of the specimens prior to the irradiation.

Within the regime of simple chemical rate theory, this problem has been solved by Damask and Dienes (DD)¹⁵ without the vacancy excess. Our treatment follows closely the DD work. The problem may be stated as follows:



Here

- V = single vacancy concentration (atomic fraction),
- i = interstitial concentration (atomic fraction),
- C = interstitial-impurity complex concentration (atomic fraction),
- $K_1 = K_2 = K = 30\nu \exp(-E/kT)$,
- I = impurity concentration (atomic fraction),
- ν = frequency factor (sec⁻¹),
- E = interstitial migration energy,
- T = temperature,
- k = Boltzman constant.

In the temperature range of interest no detrapping is assumed to occur and $K_3 = 0$. Expressions (1) and (2) give rise to the differential equations:

$$dV/dt = -KVi, \quad (3)$$

$$di/dt = -Ki(V+I), \quad (4)$$

$$dC/dt = KiI. \quad (5)$$

For our experiments, $V = i + C + q$, where q is the quenched in vacancy concentration. The initial conditions, at the beginning of random migration are

$$\begin{aligned} V &= V_0 + q, & C &= 0, \\ i &= i_0 = V_0, & I &= I_0. \end{aligned} \quad (6)$$

In this treatment radiation produced vacancies are assumed to be equivalent to quenched-in vacancies in their ability to annihilate interstitials (i.e., any vacancy-interstitial distribution function, such as that of Waite¹⁶

is neglected). Note that purely correlated close pairs are presumably excluded from consideration by the selected temperature: 21–34°K.

Equations (3)–(5) may be solved directly by the substitution of $U = C/i$, which gives an integrable expression for U :

$$U = (1+q/I_0)^{-1} \{ \exp[K(I_0+q)t] - 1 \}. \quad (7)$$

Following the approach of DD one may derive the final results for V , i , and C :

$$V = \frac{(I_0+q)(i_0+q)}{(I_0+q) + i_0 - i_0 \exp[-K(I_0+q)t]}, \quad (8)$$

$$i = \frac{(I_0+q)i_0}{(i_0+I_0+q) \exp[+K(I_0+q)t] - i_0}, \quad (9)$$

$$C = \frac{i_0 I_0 [1 - \exp[-K(I_0+q)t]]}{(I_0+q) + i_0 - i_0 \exp[-K(I_0+q)t]}. \quad (10)$$

Equations (8)–(10) have been numerically evaluated for isochronal annealing with 0.5°K steps of 5-min duration. In these calculations $\nu = 10^{18} \text{ sec}^{-1}$, $E = 0.065 \text{ eV}$ and a variety of values for i_0 , I_0 , and q where chosen. A typical result is shown in Fig. 9 where we show the isochronal recovery and the slope of the isochronal recovery for the indicated values of the parameters. In addition we indicate what we believe are four germane quantities which can be extracted from the calculation

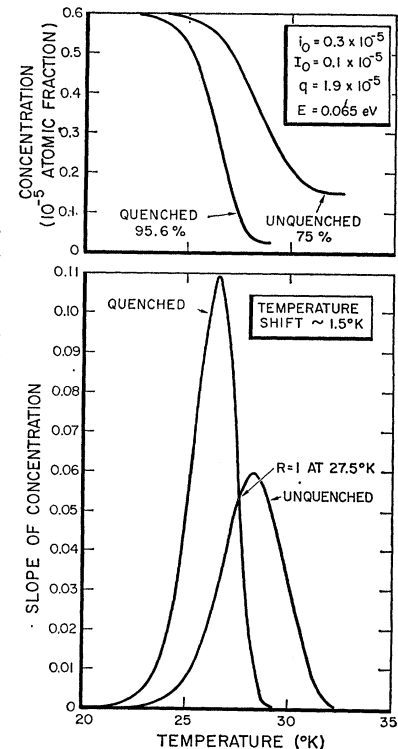


FIG. 9. Total irradiation-produced defect concentration (upper plot) and slope of defect concentration (lower plot) as a function of annealing temperature. The annealing curves were calculated from chemical rate theory (see text) for the indicated values of the initial defect concentrations and activation energy.

¹⁵ A. C. Damask and G. J. Dienes, Phys. Rev. **125**, 444 (1961).

¹⁶ T. R. Waite, Phys. Rev. **107**, 463 (1957).

TABLE II. Recovery from 21 to 32°K.

	i_0	Theory based on:		% Recovery		Temperature shift (ΔT) (°K)	Temperature at which $R=1$ (T_R) (°K)
		I_0	q	Quenched	Unquenched		
1.	0.3×10^{-5}	0.1×10^{-5}	3.9×10^{-5}	97.5	75	2.5	27
2.	0.3×10^{-5}	0.1×10^{-5}	1.9×10^{-5}	95.6	75	1.5	27.5
3.	0.3×10^{-5}	0.1×10^{-5}	0.9×10^{-5}	92.8	75	1.0	28.5
4.	0.3×10^{-5}	0.2×10^{-5}	1.8×10^{-5}	91.0	60	1.3	27.6
5.	0.1×10^{-5}	0.1×10^{-5}	0.9×10^{-5}	90.9	50	2.0	28.5
Run V. Experiment assuming							
1.	0% at 21°K			93	80	~3	26.8
2.	0% at 22°K			92	76	~3	26.8
3.	0% at 23°K			90	70	~3	26.8
	0% at 24°K and 100% at 34°K			84	50	~3	26.8

and compared to the experimental results. These quantities are the amount of recovery of the quenched and unquenched samples, the temperature shift of the annealing peak ΔT induced by the vacancy excess, and the temperature T_R at which the recovery rate of the quenched and unquenched samples are identical ($R=1$).

In Table II we summarize the numerical values of the four above-defined quantities for different values of i_0 , I_0 , and q .

B. Experiment and Comparison with Theory

We have extracted from our recovery data the same four quantities as mentioned above and tabulated their values in Table II. In order to evaluate the amount of recovery associated with free migration of the interstitial from the data, one has to assume a temperature at which the migration starts to take place. Some uncertainty is associated with the choice of this temperature. The four different choices are indicated in Table II. The transition from correlated to uncorrelated (free) migration is of course a smooth transition insofar as the isochronal-annealing temperature range is concerned. Our choice of 21, 22, 23, and 24°K was based primarily on the ratio of the slopes in Fig. 5, where a departure from the value ~ 1 takes place near 23°K. Some uncertainty is also associated with the value of ΔT since the annealing peak associated with free migration, particularly of the quenched sample, is poorly defined.

In comparing the results in Table II we note that perhaps the best agreement in the amount of recovery is achieved with parameter choice (3) in the theory and experiment (2). However, this choice leads to an underestimate in ΔT and an overestimate in T_R . Somewhat better agreement in the temperatures may be achieved with parameter choice (1) in the theory at the expense of poorer recovery agreement.

We adopt the parameter choice (3) in the theory as the one giving the better agreement with experiment. Then a qualitative explanation for the temperature discrepancy may lie in the fact that the migration of inter-

stitials proceeds more as a diffusion-limited reaction than a pure chemical-rate process. (See for example the detailed discussion by Corbett⁶ *et al.* of the Waite¹⁶ theory.) A factor which influences the stated amount of recovery is the resistivity contribution of a trapped interstitial.

There exists an independent check on the over-all consistency of the calculation by the use of the experimental results in Table I and the value of $\rho_F = \rho_i + \rho_v = 6 \times 10^{-4}$, deduced in the previous paper.¹ The resistivity decrease from 23 to 34°K in run V is

$$\Delta\rho \approx \frac{1}{3} \times 1.7 \times 10^{-9} \approx i_0(\rho_i + \rho_v), \quad (11)$$

where we have assumed the vacancy concentration to be equal to i_0 . Combining Eq. (11) with the value of ρ_F , we have $i_0 \approx 10^{-6}$. This value of i_0 is in reasonably good agreement with the various values of i_0 chosen in the theory for agreement with experiment.

We note in Table II that the parameter choices 4 and 5 differ only by initial interstitial concentrations. A reduction of a factor of 3 in the initial defect concentration results in a 25% change in the amount of the unquenched sample recovery. This amount is in excess of that which can be deduced from the experimental results of runs V and VIII in Table I. (Approximately 10% for a factor of 9 in the initial defect concentration.) Apparently the simple theory presented here is unable to quantitatively account for the dependence of the amount of recovery on the initial defect concentration. Alternatively, the amount of recovery may be influenced by dimer formation. A more refined theory is not warranted, in light of the fact that some of the fundamental quantities needed to compare theory with experiment are not well known.

VI. DISCUSSION

The experimental results and the conclusions reached on the basis of related experiments and simple calculations are consistent with a model which can be summarized in the manner shown in Fig. 10. In this figure we plot the population of defects and defect complexes formed during annealing as a function of annealing

temperature. Initially, essentially equal concentrations of interstitials and vacancies are produced by irradiation. As the annealing temperature is raised to about 23°K, approximately 70% recovery takes place almost exclusively because of nonrandom close Frenkel pair recombination. From about 23 to 30°K random interstitial annihilation takes place primarily at vacancies. Of those interstitials which are not annihilated, most are trapped, probably at impurities (dislocations are unlikely candidates in these well annealed samples), or form di-interstitials. Between 30°K and room temperature very little recovery takes place, as can be seen in Fig. 11. A small recovery stage (III) occurs near room temperature. In stage III, according to our interpretation, interstitials are released from traps and dimer migration (or dissociation) takes place. The interstitials annihilate primarily at vacancies and partly at other sinks such as grain boundaries. Finally, those vacancies which were not removed by interstitials diffuse near 600°K with an activation energy of 1.36 ± 0.08 eV to sinks.²

The recovery model presented here for platinum may be compared with several other recovery models formulated primarily for copper. The first of these has been recently proposed by Corbett¹⁷ in a review article. Corbett attributes the stage I recovery to close pairs and to free interstitial migration. Stage II is due to the release of trapped interstitials. Stage III is due to a variety of processes: the release of interstitials from deep traps, dimer migration or dissociation and vacancy migration. The trapped vacancies are released in stage IV. The only essential difference of the model presented here with Corbett's is the assignment of vacancy migration to stage IV. In platinum this assignment is firmly established.

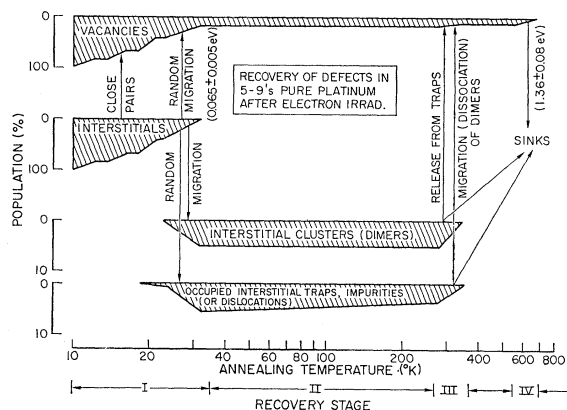


FIG. 10. Suggested recovery model in platinum after 2-MeV electron irradiation. The population of defects is plotted versus the log of the annealing temperature and the commonly used nomenclature of recovery stages. The main recovery mechanisms are indicated. Note the reduced population scale of the occupied traps.

¹⁷ J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Suppl. 7.

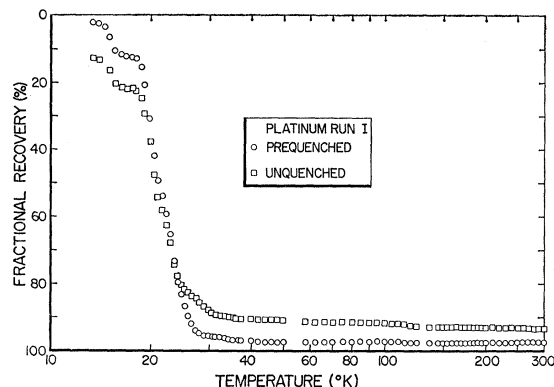


FIG. 11. The resistivity recovery as a function of annealing temperature (log scale) in run I from 13 to 300°K.

The second of these models is due to Sosin¹⁸ and Hasiguti.¹⁹ In this model close pair and free interstitial migration takes place in stage I. Some of the interstitials are trapped, the number depending on the concentration of impurities and dislocations. Stages II and III are then due to the release of interstitials from traps, stage III primarily because of the release from particular dislocation regions. Presumably stage IV is attributed to vacancy migration. Since this model was primarily based on modulus measurements, dislocation trapping was emphasized. For our well-annealed platinum samples the effective number of dislocation trapping sites is considerably less than the number of trapping sites near impurities.

The third of these models is the "two interstitial" model due to Meechan *et al.*²⁰ and Seeger.²¹ In this model the stage I recovery is due to crowdion close pairs and crowdion migration. Stage I may also have normal interstitial migration takes place in stage III and vacancy migration in stage IV. In order for the data presented here to be consistent with the "two interstitial" model would require (1) that at most 2% of the induced damage consist of a second interstitial (excluding close pairs) or (2) that a "conversion" to a second type of immobile interstitial take place at 28°K instead of, or in addition to impurity trapping or dimer formation.²² In either case the stage-III recovery would be due to the annihilation of the second type of interstitial at vacancies.

The fourth of these models has been very recently suggested by von Jan.²³ It differs fundamentally from the above three models in that *no* uncorrelated or free

¹⁸ A. Sosin, *Bull. Am. Phys. Soc.* **6**, 157 (1961).

¹⁹ R. R. Hasiguti, *J. Phys. Soc. Japan* **15**, 1807 (1960).

²⁰ C. J. Meechan, A. Sosin, and J. A. Brinkman, *Phys. Rev.* **120**, 411 (1960).

²¹ A. Seeger, in *Radiation Damage in Solids* (International Atomic Energy Agency, Vienna, 1962), Vol. 1, p. 101.

²² F. Dworschak and J. S. Koehler, *Phys. Rev.* **140**, A941 (1965).

²³ R. Von Jan, *Phys. Status Solidi* **17**, 361 (1966).

migration of either the crowdion or normal interstitial takes place below stage III, although both are created by low-energy electron irradiation in copper and aluminum. In the stage-I region the recovery is due to the correlated recombination of (100) displacements (normal interstitial) and defocused (110) long-range (LR) sequences (crowdions). The dose effects found in copper and aluminum at the end of stage I are due to the recombination of secondary pairs, where the interstitial created by an LR sequence recombines with the vacancy of another Frenkel pair, (or in a prequench case with the quenched-in vacancies). Experimentally the dose and prequench effects take place in a relatively narrow temperature range. This is explained by von Jan by assuming that the crowdion produced by a LR sequence converts into a normal interstitial, with an activation energy near 0.1 eV in copper for example, *before* it can migrate. After conversion the normal interstitial, of course, recombines with a vacancy if the recombination energy is less than the conversion energy. Uncorrelated or free migration of the normal interstitial takes place in stage III. The data presented here are qualitatively consistent with the model proposed by von Jan.

von Jan explains the relatively small stage-I recovery

in gold as being due to the absence of (110) displacements. Consequently in light of the above discussion one would expect the displacement processes in platinum and gold to be different. From the results of the previous paper we see that this does not seem to be the case for $45 \text{ eV} < T_m < 70 \text{ eV}$. On the other hand the comparison of the gold and platinum damage rates in the preceding paper may not extend to sufficiently large values of T_m to permit a conclusive comparison on this matter. Clearly higher energy irradiation of gold is desirable.

In conclusion, the data presented here do not lead to an unambiguous choice between the various recovery models discussed in this paper.

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Derivation of Kondo Anomalous Scattering from the Anderson Dilute-Alloy Model

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The Anderson extra-orbital dilute-alloy model is shown to lead to the same type of anomalous conduction-electron scattering found by Kondo from the s - d exchange model. This is accomplished by evaluating the d -state Green's function to fourth order in the s - d mixing potential and in the limit of large repulsion between two d -state electrons, using equation-of-motion techniques.

1. INTRODUCTION

IN a recent paper¹ (hereafter denoted I), the author showed that Anderson's dilute-alloy model² yields a Curie-law magnetic susceptibility when the mutual repulsion U between two electrons in the extra " d " orbital is large, and the d -state width is small compared with its binding energy. This result demonstrates that a virtual bound state can display at least one of the properties associated with a truly bound spin. It is known, however, that a truly bound spin in a metal displays another important property—the anomalous scattering of the conduction electrons found by Kondo.³ In this paper, we extend the calculation of I to the next

order, and demonstrate the existence of the Kondo anomalous scattering term for the Anderson model. Furthermore, the coefficient of this term is just that given by substituting the exchange constant found by Schrieffer and Wolff⁴ through a canonical transformation of Anderson's Hamiltonian into Kondo's result.³

We do not attempt in this paper to reproduce the results of the more sophisticated treatments of Kondo's model,⁵⁻⁹ but merely those of the perturbation-

⁴ J. R. Schrieffer and P. A. Wolff, *Phys. Rev.* **149**, 491 (1966).

⁵ Y. Nagaoka, *Phys. Rev.* **138**, A1112 (1965).

⁶ H. Suhl, *Phys. Rev.* **138**, A515 (1965); *Physics* **2**, 39 (1965); *Phys. Rev.* **141**, 483 (1966); H. Suhl and D. Wong (to be published).

⁷ A. A. Abrikosov, *Zh. Eksperim. i Teor. Fiz.* **48**, 990 (1965) [English transl.: *Soviet Phys.—JETP* **21**, 660 (1965)]; *Physics* **2**, 5 (1965); **2**, 61 (1965).

⁸ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **34**, 204 (1965).

⁹ K. Yosida, *Phys. Rev.* **147**, 223 (1966).

¹ D. R. Hamann, *Phys. Rev. Letters* **17**, 145 (1966).

² P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

³ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32**, 37 (1964).