were the same as for para-D_2.

In summary, these new Raman spectra for oriented crystals give an unambiguous identification of the single-libron modes and remove all former reservations in assigning the $Pa3$ structure to the orientationally ordered phase of pure orthodydrogen and paradeuterium.

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[11]The results appropriate to the present experimental arrangement can be easily obtained from their results by noting that the inverse of the coordinate transformation operator is obtained by the substitutions $\varphi \rightarrow -\psi$, $\theta \rightarrow -\theta$, and $\psi \rightarrow -\varphi$. In addition, a number of algebraic errors had to be corrected.

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Evidence for the Dissociation of Close Pairs Produced in Platinum at Temperatures Above Stage I*

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Experimental data are interpreted as evidence that with increasing irradiation temperature above Stage I in metals there is an increasing probability that close pairs will dissociate. The dissociated partners contribute to the damage produced during elevated-temperature irradiations in the same way as free defects produced otherwise.

When a close Frenkel pair is produced at a high temperature there is a significant probability that the interstitial will jump away from its vacancy partner towards a more stable position. Let E_r be the activation energy required for an interstitial to make a jump closer to its vacancy partner towards possible recombination. Similarly, let E_d be the activation energy for the interstitial to jump away from its partner towards possible dissociation. The respective probability for each type of jump at temperature T is proportional to $N_r \exp(-E_r/kT)$ or $N_d \exp(-E_d/kT)$, where N_r and N_d are the number of equivalent sites associated with either type of jump. The fraction of interstitial jumps towards dissociation then is

$$f_d = \frac{N_d \exp(-E_d/kT)}{N_d \exp(-E_d/kT) + N_r \exp(-E_r/kT)}. \quad (1)$$

If $E_d - E_r \equiv \Delta E$ and $N_r/N_d \equiv \gamma$ then,

$$f_d = [1 + \gamma \exp(\Delta E/kT)]^{-1}. \quad (2)$$

For many metals the low-temperature recovery-rate spectra are known for several types of irradiations, and in some cases values of E_r have been measured for particular types of close pairs. On the other hand, no values for E_d, and hence ΔE, have been measured. Since values of ΔE are unknown, we assume $\Delta E \simeq 0.2E_r$, and using a typical value for E_r of 0.1 eV the following values for f_d are obtained with Eq. (2):

T (°K)	f_d
30	0.00033
100	0.09
300	0.26
1000	0.44
∞	0.50

A value of $\gamma = 1$ was used to calculate the above examples. Values of γ less than 1 are more realistic and would enhance dissociation, reducing the temperature required to produce a given

value of f_d.

The following are additional considerations of the behavior of defects produced in metals at elevated temperatures (generally above Stage I):

(1) If an interstitial makes a successful jump away from its paired vacancy partner, the probability of making another such jump towards freedom becomes greater and must be recalculated using a smaller value of ΔE. Alternatively, a single jump of an interstitial towards its partner does not necessarily insure recombination as it would at lower temperatures (such as during study after low-temperature irradiation). Thus a proper mathematical description of recombination and dissociation of paired defects in metals at elevated temperatures is more complicated than Eq. (2).

(2) At temperatures only slightly above those corresponding to Stage I the most weakly bound pairs with interstitials having the smallest values of ΔE will contribute most to the enhancement of damage production. Additional enhancement by this close-pair species is expected to diminish with increasing temperature when its value of f_d approaches 0.5 [or more exactly, $1/(1+\gamma)$]. The contribution of other species having larger values of ΔE may then become more significant at higher temperatures. This suggests that the temperature dependence of defect production, due to pair dissociation, may not be discribable in simple terms.

(3) Theoretically, at sufficiently high temperatures, even subthreshold pairs (presumed to have high ΔE values) have a chance for dissociation.

(4) It is, of course, assumed that when a close pair dissociates the resulting free defects are indistinguishable from those produced directly by the irradiation, and both types can migrate to those destinations where they remain as observable damage.

This report gives preliminary experimental data interpreted as evidence for the dissociation of close pairs in platinum. This metal was chosen for the present study because it shows very little thermal recovery of damage following Stage I (about 60°K) up to about 300°K (see Fig. 1), thus providing a wide temperature range for damage production studies which is not greatly influenced by simultaneous thermal annealing of damage. The study was made using thermal neutrons which produce a large Stage I population (see Fig. 1), thus improving the chances to observe the effects of close-pair dissociation.

Similar effects have been reported in semiconductors.[1-4]

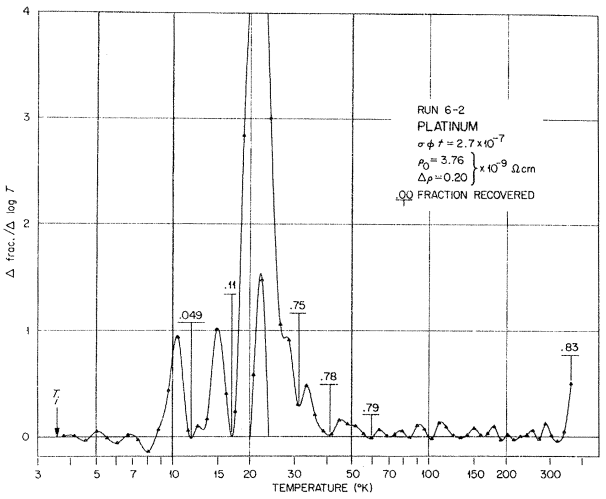

FIG. 1. Isochronal recovery of thermal-neutron damage in platinum irradiated at 3.6°K. The isochronal program used temperature increments smoothly tapered from $\Delta T = 0.1T$ at the lowest temperature to $\Delta T = 0.05T$ at the highest. Because of the relatively coarse program at low temperatures a first order peak (I-*C*) commonly seen at 22°K is not visible here. Other thermal-neutron–damage studies we have made using finer programs show this peak precisely as seen by others. For thermal-neutron damage its relative population is represented by a peak height nearly equal to the I-*D* (center at 28°K) and appears as a splitting of the large peak seen in this figure.

The specifications of the 0.010-in.-diam platinum-wire sample, which had been previously irradiated, are described in an earlier report[5] along with all experimental arrangements, instrumentation, and irradiation conditions. The measured resistance ratio of the specimen at the beginning of this study was 2640. All resistance measurements were made in liquid helium at 3.4°K. The sample was irradiated at various temperatures in helium gas at 3 atm pressure to the same irradiation dose ($\pm\frac{3}{4}\%$) of $(4.9\times10^{16})n/\mathrm{cm}^2$ thermal neutrons, which produced a capture-event concentration of 4.3×10^{-7}. Prior to the irradiation at each temperature the sample was annealed for 15 min at 406°K. It is known that not all damage in platinum recovers at this temperature,[6] and the possible influence of irradiation doping in this study is discussed later.

The circles in Fig. 2 show the residual resistivity increase measured after each irradiation at the indicated temperature. Numerals adjacent to the circles indicate the sequence of irradiations, which was random. Except for the data point (3) all others show a consistent trend to-

wards increasing damage production with increasing irradiation temperature, which is in agreement with the proposal made earlier. The temperature of the third irradiation (315°K) is seen in Fig. 1 to be immediately adjacent to a prominent recovery rate peak. The failure of this point to be consistent with the remainder of the data is attributed to the occurrence of substantial thermal annealing during the 5-h standard irradiation. In spite of this, the data point still shows a net increase in damage production at 315°K over that measured at the lowest temperature of 83°K.

Two accompanying effects are believed to occur for which reasonable corrections to the raw data (circles) are possible. These effects, discussed in turn, are the slight thermal annealing over the temperature range studied and irradiation doping. Even for platinum, thermal recovery over the range studied (83-280°K) is not completely nil. For the standard dose the small amount of resistivity recovery between these temperatures, according to the isochronal program of 5-min pulses seen in Fig. 1, was 5.2×10^{-12} Ω cm.[7] To place the results of each irradiation upon a more comparable basis by reducing the influence of thermal annealing, a single 5-min annealing pulse at 315°K was made after each postirradiation measurement. The results of measurements after each 315°K pulse are shown as squares in Fig. 2.

Since the 15-min anneal at 406°K prior to each irradiation does not remove all damage in platinum, it is reasonable to expect an irradiation doping effect. Irradiation doping effects have been seen in many metals, including platinum. Evidence of this effect in the present work is noted for irradiations (2) and (6), which were both made at 83°K. The difference in damage production between these two runs, although small, is beyond experimental error and is in the usual direction observed for irradiation doping. To adjust the present data on a self-consistent basis we have assumed the irradiation doping effect to increase uniformly with each successive irradiation according to the rate established by the difference between runs (2) and (6). When applied to the square data points these small corrections give the data points designated by crosses, through which straight-line segments have been drawn. Although not an overriding influence, the precise overall effect upon this study of all the irradiation doping this sample has received during its history is difficult to assess. The present data show clearly, however, that irradiation doping acts to diminish the effects of close-pair dissociation we have attempted to study.

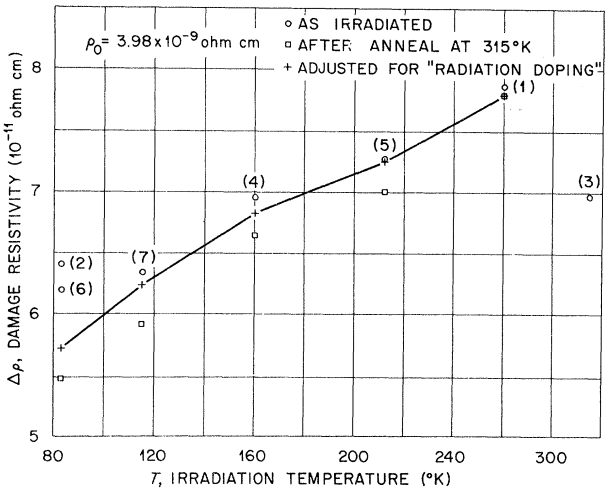

FIG. 2. Increments of thermal-neutron–damage resistivity produced at various temperatures by the same irradiation dose (4.3×10^{-7} atomic concentration capture events). It is estimated that on the average each capture event produces roughly about ½ Frenkel pair at 3.6°K of which about 80% anneal below 83°K.

It is well known that damage-production curves of metals irradiated above Stage I are generally not linear and for some a square root dependence upon dose has been observed in the region of Stage II, where the present study was made. Because of this nonlinear behavior the most precise description of the present study would be given in terms of initial damage-production rates. In the present work damage increments were measured, and their use in approximating damage rates must necessarily give values smaller than actual initial rates. To relate damage increments to initial damage rates we note that the precise behavior of a damage-production curve depends upon the defect-trap concentration, e.g., impurities, and that the initial slope changes slowly over the range where defect concentrations are small compared with trap concentrations. Since damage-resistivity increments in the present work were only about 2% of the initial residual resistivity ρ_0 (see Fig. 2), a comparison of the incremental values with actual initial rates would probably not show serious disagreement. Thus we conclude that the 36% enhancement observed at 280°K over that at 83°K is probably a minimum value.

Using the percentage recovery data employed to produce the recovery rate spectrum in Fig. 1, we determined that the greater damage produced at 280°K over 83°K is about 7% of the total damage that would have been produced by irradiation at 3.6°K. All of the damage that can be imagined

to participate in the dissociation process must come from Stage I, excluding Stage I-E, which represents the recovery of defects which are already free.[8] For thermal neutron damage in platinum it is estimated from Fig. 1 that this is about 70% of the total damage (the structure at 28°K is known to be the I-E peak). It is estimated, then, that for an irradiation temperature of 280°K about 10% of the available Stage I defects survived after dissociation. It is possible that a somewhat higher percentage may have dissociated successfully but some were lost due to annihilation instead of being trapped to remain as resistivity increase.

Equation (2) is based on the probability of a jump originating at a single species of close pair. This formulation suffices to describe dissociation in the simplest imaginable model in which a single jump of the interstitial towards its vacancy partner insures recombination, or a single jump away insures freedom. However, such a model implies an unrealistically abrupt change in the magnitude of ΔE (from zero to a very large value in two adjacent lattice spacings), quite at variance with the behavior of any reasonable interatomic potentials.

Consideration of just the next logical degree of complication beyond the single-stage model, namely a one-dimensional two-stage model, has shown that perhaps either model may not be a bad approximation. With reasonable assignments of the values of required parameters either model gives results similar to the experimental data. Both suggest ΔE values in the range 0.01 to 0.02 eV. More detailed analysis will be presented later with the results of additional experiments now in progress.

One important consequence of the dissociation process is that with increasing irradiation temperature above Stage I the fraction of all produced defects which become free also increases. Since damage retained above Stage I is the result of free defects, increasing the irradiation temperature gives an effect equivalent to increasing the irradiation flux. The possible implications of this effect in understanding the behavior of damage in reactor materials are being considered.

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[8]Current theory of correlated pair recovery in Stage I-D assumes that initially $\Delta E = 0$ for the interstitial partner. Recovery in I-D is assured when as a result of diffusion the interstitial reaches a point where $\Delta E \neq 0$ with respect to its own vacancy. When produced at temperatures above Stage I, however, the dissociation mechanism predicts that a diffusing correlated interstitial may sometimes escape its vacancy even though a positive value of ΔE is momentarily established. The effect is to reduce the correlation between partners and allow more of them to diffuse as free defects.