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Anelasticity study of self-interstitials in tungsten

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The internal friction and dynamic modulus of W single crystals and polycrystal were measured after fast-neutron irradiation near liquid-helium temperature. Two prominent relaxation peaks were observed at 8 and 27 K (at vibrational frequencies ≈ 500 Hz). The 8- and 27-K peaks annealed out, respectively, in the recovery stages I (~ 18 K) and II_a (~ 30 K), increased in height almost linearly with irradiation dose, and were not affected by preirradiation doping. Their orientation dependence suggests that the defects of these peaks have a maximum strain field along the $\langle 110 \rangle$ crystallographic direction. From these results it is proposed that the origin of these two peaks is a stress-induced rotation of free $\langle 110 \rangle$ split-type self-interstitials (8-K peak) and of di-interstitials (27-K peak). Anisotropy ratios and activation energies for rotation of these defects are determined. Many minor peaks were also observed in the temperature range 7 to 310 K. Properties of these peaks suggest that some of them are attributable to interstitials trapped by impurity atoms and the others to interstitial clusters. These results are discussed in comparison with the resistivity recovery stages.

I. INTRODUCTION

Whereas the low-temperature recovery spectra of W observed by electrical-resistivity measurements are somewhat variant in several investigations, in his review paper Nihoul[1] included the recovery stages below 100 K in stage I and this stage was divided into five substages: namely, I_1 (~ 15 K), I_2 (~ 28 ~ 30 K), I_3 (~ 40 K), I_4 (~ 60 K), and I_5 (~ 80 K). This nomenclature means, at least implicitly, that a free migration of self-interstitials occurs at ~ 80 K (or ~ 60 and ~ 80 K) and close-pair recombinations occur below this substage. In a previous paper,[2] it was shown that a free migration of self-interstitials is considered to occur at ~ 15 K (or more accurately, recovery temperature centered at ~ 18 K) and accordingly, the above nomenclature does not seem proper now. It seems more proper to name these stages as I (~ 18 K), II_a (~ 30 K), II_b (~ 40 K), II_c (~ 60 K), and II_d (~ 80 K). The evidence was supplied by the internal-friction experiments, i.e., the dislocation pinning by self-interstitials in low irradiation doses and the Snoek-type peak of the self-interstitials in high irradiation doses. The latter part of the work, i.e., the study of relaxation peaks associated with self-interstitials in W, will be described in detail in this paper.

DiCarlo, Snead, and Goland[3] studied in detail the relaxation peaks in electron-irradiated W, but only above 20 K. They found a relaxation peak at ~ 30 K (resonant frequency of ~ 600 Hz) and attributed it to the stress-induced ordering of the interstitial members of close Frenkel pairs. Further, from the dependence of the relaxation strength on stress direction, the interstitials were determined to be $\langle 110 \rangle$ split interstitials. In the present work, similar measurements were made on W irradiated by neutrons near liquid-helium temperature. Two main relaxation peaks owing to $\langle 110 \rangle$ split interstitials were observed at 8 and 27 K (~ 500 Hz). These two types of interstitials were found to perform a long-range migration at around 18 and 30 K, respectively.[2] A detailed study on these and other relaxation peaks led us to a rather different assignment of defects and recovery stages from that of DiCarlo *et al.*

It should be noted here that there exists a striking analogy between Mo and W. In Mo, $\langle 110 \rangle$ split interstitials of two types cause two relaxation peaks at 12 and 39 K, respectively.[4,5] As a matter of fact, the present work on W was motivated by these findings on Mo.

II. EXPERIMENTAL PROCEDURE

Plates of a single crystal were cut out of single-crystal rods (nominal purity 99.999%) purchased from Materials Research Corporation and shaped into specimens. The specimens have a size of about $0.2 \times 3 \times 20$ mm^3 with a step, one end being thicker to ensure a rigid gripping in the specimen holder. They were etched and annealed at about 2000 °C in a vacuum of better than 2×10^{-8} Torr. One polycrystalline specimen was also measured to find out the effect of impurities. Specifications of specimens are listed in Table I. As shown in the table, the residual resistivity ratios after annealing were varied from 20 000 ($\langle 111 \rangle$ single-crystal) to 55 (polycrystal). The procedures of irradiation and postirradiation measurements were similar to those described elsewhere.[6] Briefly, in the low-temperature in-pile irradiation facility liquid-helium temperature loop in Japan Atomic Energy Research Institute, the specimens were irradiated near liquid-helium temperature by neutrons of nearly fission spectrum with 1.15×10^{12} neutrons/cm^2 sec (> 0.1 MeV).

After irradiations, the specimens were transferred to the measuring cryostat without any

TABLE I. Specifications of specimens.

Specimens	Direction[a]	RRR[b]	Pre-irrad. treatment	Irrad.	Remark
W-1	⟨100⟩	$8.0 \sim 8.2 \times 10^3$	annealed	Run 1: 30 h Run 2: 90 h Run 3: 10 h	Effect of doping
W-2	⟨100⟩		2-h doped[c]	30 h	
W-3	⟨100⟩		0.5-h doped[d]	10 h	
W-5	⟨100⟩		15-h doped[d]	30 h	Orientation dependence
W-6	⟨111⟩	2.0×10^4			
W-7	⟨110⟩	2.4×10^3			
W-8	polycrystal	55	annealed	27 h	Effect of impurity

[a] Long axis of plates is parallel to this direction within 1° (checked by x rays).
[b] Residual resistivity ratio.
[c] Doped by irradiation at room temperature.
[d] Doped by irradiation at low temperature and annealed at room temperature.

warmup, and the internal friction and dynamic modulus were measured during warmups. The flexural vibration of the specimens (~ 500 Hz) was both excited and detected by electrostatic means. The internal friction Q^{-1} was obtained from a free decay and also from a drive force at constant amplitude of vibration. The change in elastic modulus ($\Delta M/M \approx -2\Delta P/P$) was measured from a period of vibration at resonance P. The maximum strain amplitude of the specimens was of the order of 10^{-6} and the warmup rate during measurements was normally $0.5 \sim 1$ K/min.

III. EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) show the results of internal friction and dynamic modulus for the ⟨100⟩ single-crystal specimen during warmup after the second irradiation[7] at ~ 5 K for 90 h. Two pronounced relaxation peaks at 8 K (8-K peak) and 27 K (27-K peak), and a number of smaller ones are seen in Fig. 1(a). As is expected for a relaxation peak, their recoveries are accompanied by the recovery of the modulus defect as shown in Fig. 1(b). Comparing the results of the first irradiation for 30 h,[2] there appears to be no effect of the previous irradiation on the behavior of the peaks. The minor peaks are observed at about 7, 12, 23, 34, 40, and 50 K. A peak at ~ 30 K which in Fig. 1(a) is buried in the higher-temperature side of the 27-K peak, can be observed clearly in measurements with different warmup schedules (not shown here). There is one more peak at ~ 60 K which is too small to be seen in this figure. The very small peak at ~ 7 K appears only for high dose and grows transiently during annealings. In the ⟨100⟩ and ⟨111⟩ single crystals of high purity, there appears to be no other relaxation peaks observable up to

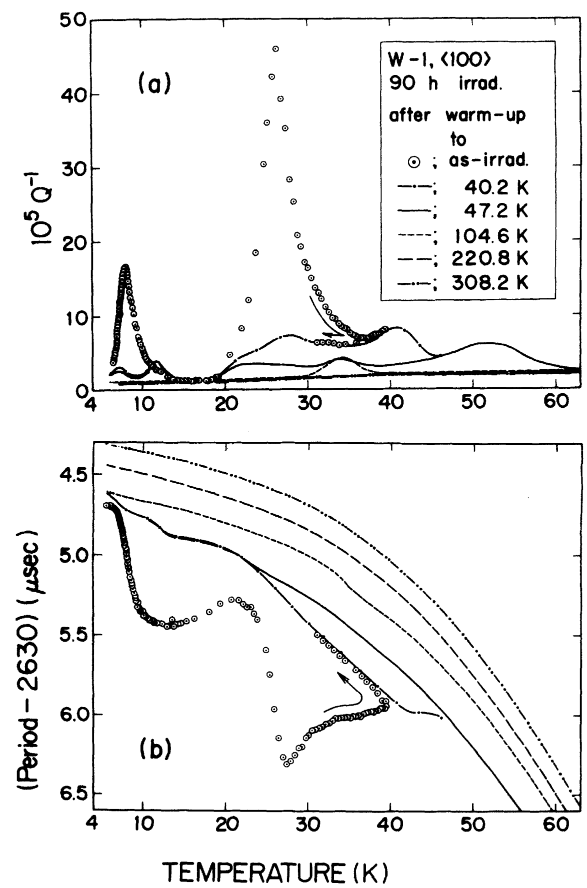

FIG. 1. (a) Internal friction and (b) dynamic modulus of the ⟨100⟩ single-crystal W during warmup after fast-neutron irradiation near liquid-helium temperature for 90 h. Dynamic modulus was represented by the period of resonant vibration, the ordinate showing the period (in μ sec) minus 2630 μ sec. Warmup runs were made to successively higher temperatures as shown in the figure.

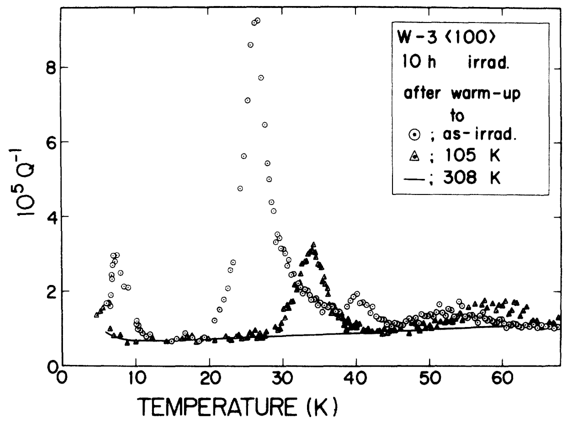

FIG. 2. Internal friction of the ⟨100⟩ single-crystal W during warmup after fast-neutron irradiation near liquid-helium temperature for 10 h. Warmup runs were made to successively higher temperatures as shown in the figure.

310 K. Figure 2 shows the results for a 10-h irradiation. Compared to the results of the third irradiation of the specimen W − 1, which is not shown here, again no effect of radiation doping (total 120-h irradiation, then annealed at room temperature) was observed on the peaks except that the peak at ~ 34 K (34-K peak) becomes much smaller after the third irradiation.

The results for the ⟨110⟩ specimen irradiated for 30 h are shown in Fig. 3, where the 8- and 27-K peaks are much smaller, but the 34-K peak appears to be more pronounced when compared to the ⟨100⟩ specimen. Above 60 K and up to 310 K, only one peak at ~ 137 K (137-K peak) is seen [see Fig. 10(b)]. In the ⟨111⟩ specimen (not shown here), all the peaks observed are much smaller than in

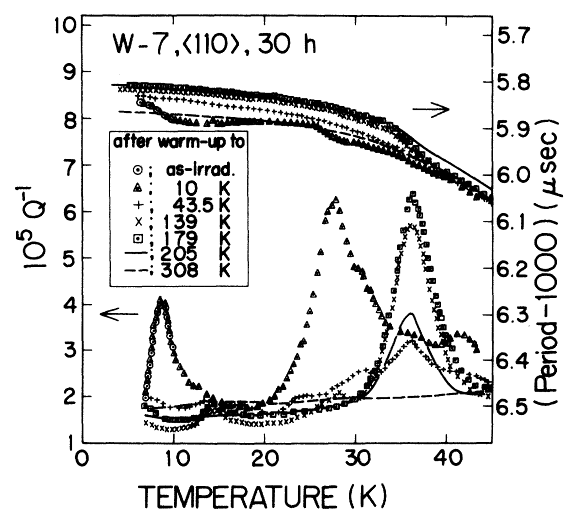

FIG. 3. Similar as Fig. 1, but for the ⟨110⟩ single-crystal W irradiated for 30 h.

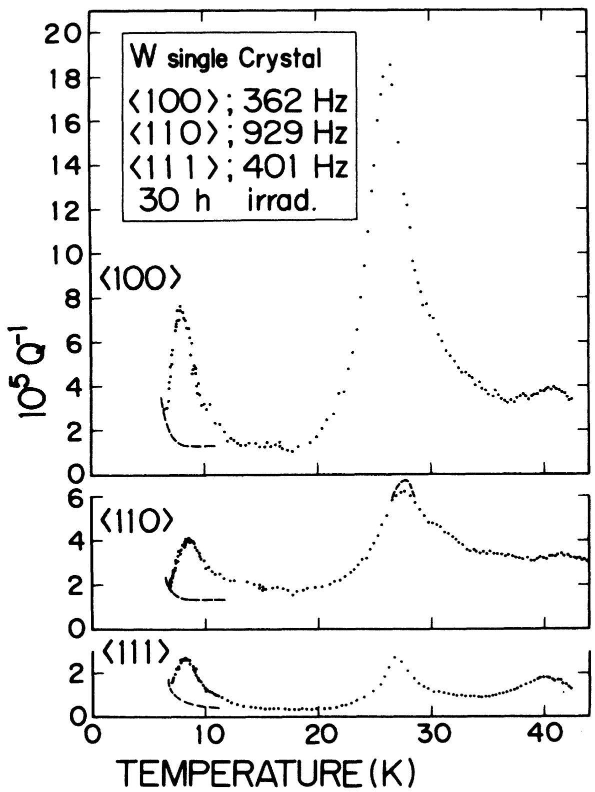

FIG. 4. Internal friction vs temperature curves for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ single-crystal specimens during warmup after fast-neutron irradiation near liquid-helium temperature for 30 h. All specimens were irradiated at the same time. Dashed line over the 27-K peak of the ⟨110⟩ specimen is extrapolated from the lower-temperature side of the peak. Dashed lines under the 8-K peak show the estimated background components caused by the residual helium gas.

the ⟨100⟩.

In order to study the orientation dependence of the 8- and 27-K peak heights, the ⟨100⟩, ⟨110⟩, and ⟨111⟩ specimens were irradiated simultaneously in one capsule for 30 h. The results are shown in Fig. 4. In the ⟨110⟩ specimen, because of its higher resonant frequency, the 27-K peak appears at a little higher temperature and decays during measurements faster than the other two specimens. The errors due to this effect were corrected by extrapolation from the lower-temperature side of the peak as shown by the dashed line in the figure. The stress direction of the ⟨100⟩ specimen is ⟨100⟩, and similarly for ⟨110⟩ and ⟨111⟩. Ratios of the relaxation strengths of the two peaks for ⟨100⟩ stress ($\Delta_E^{\langle 100\rangle}$), ⟨110⟩ stress ($\Delta_E^{\langle 110\rangle}$), and ⟨111⟩ stress ($\Delta_E^{\langle 111\rangle}$) obtain from these results are; for the 8-K peak

$$\Delta_E^{\langle 110\rangle}/\Delta_E^{\langle 100\rangle} = 0.426 \pm 0.066 \;, \qquad (1)$$
$$\Delta_E^{\langle 111\rangle}/\Delta_E^{\langle 100\rangle} = 0.327 \pm 0.029 \;,$$

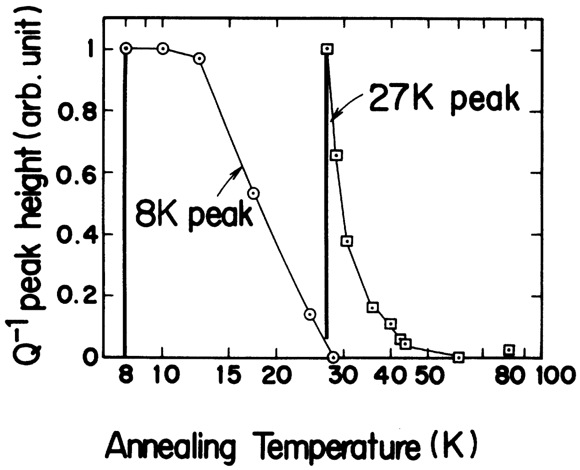

FIG. 5. Normalized peak heights of the 8- and 27-K peaks vs annealing temperatures. Since the specimens were cooled down immediately after having been warmed up to each indicated temperature, strictly, these curves represent only approximate isochronal recovery curves.

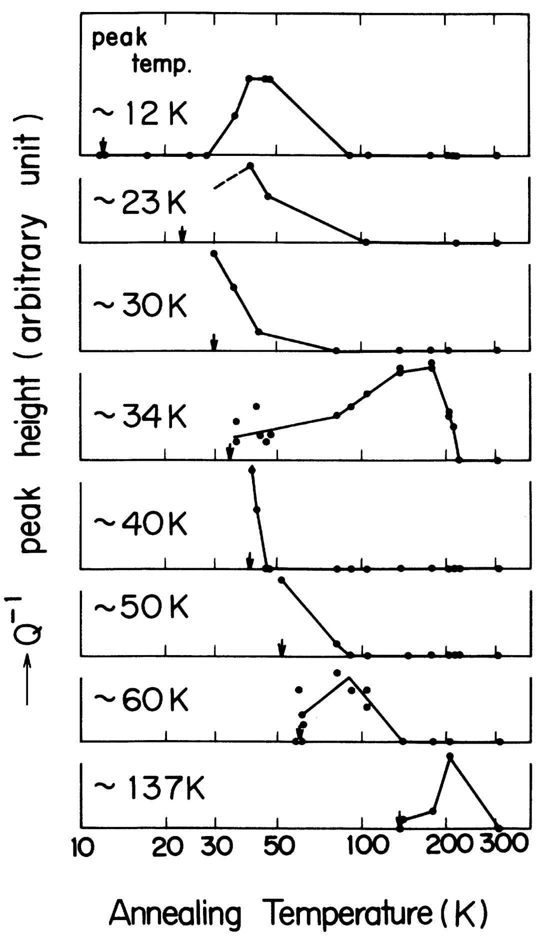

FIG. 6. Similar as Fig. 5, but for the minor peaks observed in single-crystal W.

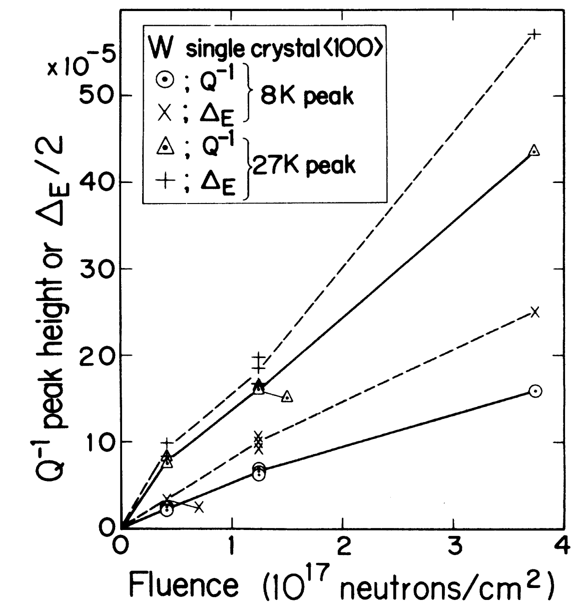

FIG. 7. Peak heights (Q^{-1}) or the relaxation strengths deduced from the modulus defect (Δ_E) vs irradiation doses for the 8- and 27-K peaks.

and for the 27-K peak

$$\Delta_E^{\langle 110\rangle}/\Delta_E^{\langle 100\rangle} = 0.290 \pm 0.051\ ,$$
$$\Delta_E^{\langle 111\rangle}/\Delta_E^{\langle 100\rangle} = 0.133 \pm 0.015\ . \tag{2}$$

A change in the peak heights during annealings is shown in Figs. 5 and 6 for the peaks observed in the single-crystal specimens. In Fig. 5, it is seen that the 8- and 27-K peaks anneal out in the broad temperature range centering at ~ 18 and ~ 30 K.

In Fig. 7, the peak heights and the relaxation strengths measured from the modulus defects ($\Delta M/M$) against irradiation doses are shown. The half-width of the 8-K peak is about twice as large as that of the hypothetical single relaxation peak, so that the $\frac{1}{2}\Delta_E$ estimated from $\Delta M/M$ is larger than the actual peak height. For the 27-K peak, the estimation of $\frac{1}{2}\Delta_E$ from $\Delta M/M$ includes a large uncertainty because of the overlap of the modulus change owing to recovery of the 8-K peak at lower temperatures and a rapid decay of the peak at higher temperatures. However, the peak-height increase could be said to be roughly proportional to the irradiation doses.

Arrhenius's plots of vibrational frequencies against inverse peak temperatures for the 8-, 27-, and 30-K peaks are shown in Figs. 8 and 9. The plot of the 8-K peak shows a great scatter, but the straight line with the attempt frequency $\nu_0 \approx 1\times 10^{14}$ sec^{-1} and the activation energy $E_R \approx 17$ meV would not be unreasonable. The attempt frequencies and activation energies for the 27-K peak ($\nu_0 \approx 1\times 10^{14}$

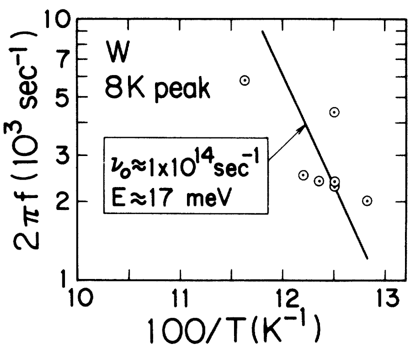

FIG. 8. Arrhenius's plot of resonant frequencies (f) of specimens vs peak temperatures for the 8-K peak.

sec^{-1} and $E_R \approx 56$ meV), and for the 30-K peak ($\nu_0 \approx 1 \times 10^{14}$ sec^{-1} and $E_R \approx 62$ meV) are obtained from the straight lines in Fig. 9. In Fig. 9, the peak found by DiCarlo *et al.*[3] at ~ 30 K is also plotted.

In order to study the effect of impurities, the impure polycrystalline specimen was similarly measured. The results are shown in Figs. 10(a) and 10(b), together with the results of the ⟨110⟩ specimen at higher temperatures. In the polycrystalline specimen, the 8- and 27-K peaks appear even smaller than those of the ⟨111⟩. Further, the 8-K peak appears to show a transient growth during annealing. Since in all of the single-crystals studied in the present work, the 8-K peak simply decayed around 18 K, the origin of the peak which grew during annealing seems to be different from that of the 8-K peak observed immediately after irradiation. The 137-K peak only appears in the polycrystalline and ⟨110⟩ specimens. The 34- and 137-K peaks are largest in the polycrystalline sample. Furthermore, the polycrystalline sample shows many other minor peaks which are absent in the single-crystal ones. These are at around 14, 54, 74, 82, and 97 K. As will be shown later,

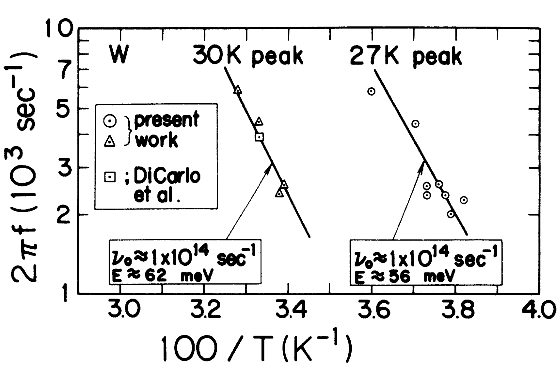

FIG. 9. Similar as Fig. 8, but for the 27- and 30-K peaks. DiCarlo *et al.* estimated the true peak temperature of their peak observed at ~30 K to be 31.9±2.0 K, but 30 K was used here.

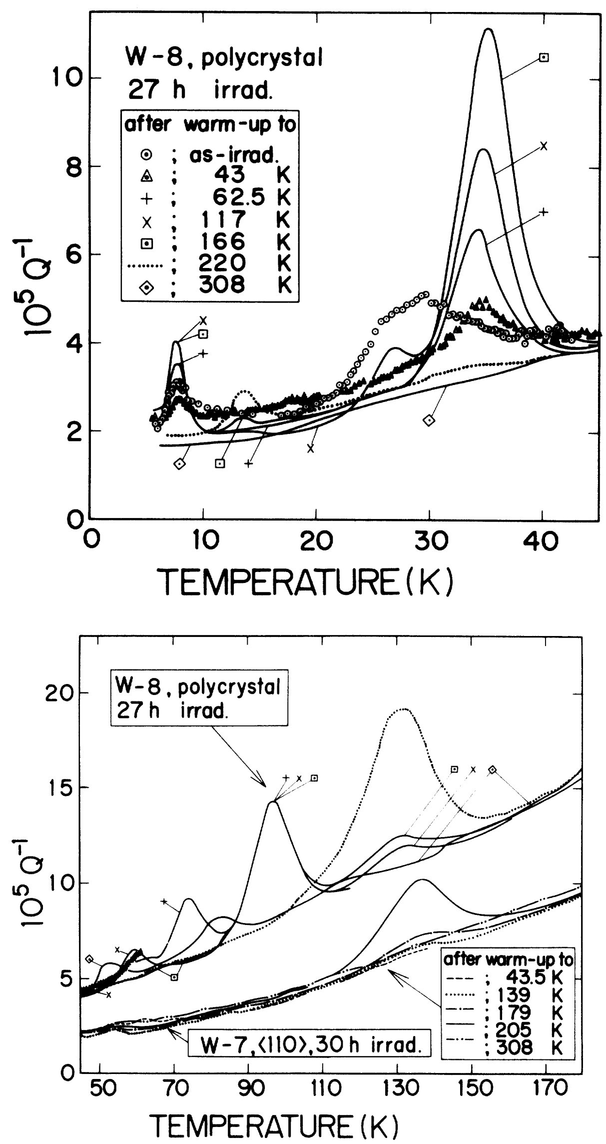

FIG. 10. Internal friction of the polycrystalline W during warmup after fast-neutron irradiation near liquid-helium temperature for 27 h. Warmup runs were made to successively higher temperatures as shown in the figure. (a) For low-temperature region and (b) for high-temperature region. In (b), the results of the ⟨110⟩ single-crystal W irradiated for 30 h are included for a comparison purpose.

all these peaks are considered to be related to the effects of impurities.

IV. DISCUSSION

A. 8- and 27-K peaks

1. Origin of the peaks

The main features of the 8- and 27-K peaks are summarized as follows: (a) These peaks anneal out in the recovery stages I (8-K peak) and II_a

(27-K peak), where dislocation pinning through long-range migration of point defects was observed for low-irradiation doses.[2] (b) Preirradiation doping has no essential effect on the peaks, at least in the radiation-doping ranges studied in the present work. (c) The peak heights are roughly proportional to doses or defect concentrations at least in the present dose range. (d) Arrhenius's plots of the peak temperatures are not unreasonable as phenomena caused by a motion of point defects ($\nu_0 \approx 10^{14}$ sec^{-1}). (e) From the orientation dependence of the peak heights,[3] it can be concluded that the defects associated with both peaks have a maximum strain field along a $\langle 110\rangle$ crystallographic direction. (f) They have a good analogy with the 12- and 39-K peaks of Mo.[5]

Case (b) excludes the possibility that the peaks are associated with dislocation motion. Cases (a) and (d) suggest that the 8- and 27-K peaks are associated with the stress-induced rotation (without migration) of point defects of the stages I and II_a, respectively. Case (c) suggests that they are rather simple point defects. Then, with case (e), one can conclude that these defects are $\langle 110\rangle$ split interstitials of two different types.

Since stage I is the lowest stage where a long-range migration is observed, it is natural to assign the free migration of $\langle 110\rangle$ split interstitials to stage I and the rotation of these free interstitials to the 8-K peak (see Ref. 8 for further discussion).

Then, the defects of the 27-K peak or stage II_a should be free interstitials of another type, or interstitials trapped by either other interstitials or impurity atoms. The interstitials of the extended types proposed by Afman[9] and Moser[10] are not reconcilable with the $\langle 110\rangle$ symmetry. Free interstitials of a different type with $\langle 110\rangle$ symmetry do not seem possible in the body-centered-cubic (bcc) structure. Therefore, stage II_a defects should be trapped interstitials.

In neutron irradiation, high-energy primary knock-on atoms produce cascades where the local defect density would be high enough to give a good chance for interstitials to form di-interstitials. Larger clusters would also be formed but much less in number. Therefore, the di-interstitials are probable as the defects of the 27-K peak. Since the local high density in the cascades would remain almost the same during an increase in irradiation doses as long as an overlap of the cascades does not come in, the number of di-interstitials, i.e., the 27-K peak height, would increase linearly with irradiation dose [case (c)].

Finally, let us examine the possibility of trapping by impurity atoms for the 27-K peak. According to Schultz,[11] the concentration of metallic impurities would be estimated as $\lesssim 40$ atomic (at.)ppm for a residual-resistivity ratio (RRR) of ~8 000 and $\lesssim 15$ at.ppm for a RRR of ~20 000. On the other hand from the resistivity measurements[12] the concentration of Frenkel defects after a 30-h irradiation is estimated to be 40~80 ppm (see Sec. IV A 2). Therefore, for the 27-K peak in a specimen with a RRR of ~20 000, or in the specimen with a high-irradiation dose, the impurity trapping is not impossible, but di-interstitial seems to be more probable. The estimation of impurity concentrations from RRR is, however, rather uncertain,[13] and the possibility of impurity trapping can not be denied by the argument based on the RRR. As will be shown later, however, there is evidence which suggests di-interstitials for stage II_a defects (see Sec. IV B).

The 8- and 27-K peaks in the impure polycrystalline specimen immediately after irradiation are much smaller even than in the $\langle 111\rangle$ specimen. This result can be simply explained by the fact that many interstitials are formed and trapped near impurities through a dynamic focusing collision process and thus, the peaks are arrested in the impure specimen.

2. *Defect properties*

For defects in cubic crystals, the relaxation strength for an applied uniaxal stress along a $\langle hkl\rangle$ crystallographic direction can be given by[3,14]

$$\Delta_E^{\langle hkl\rangle} = \frac{C v_0 E^{\langle hkl\rangle}}{9kT}\,\Psi^{\langle hkl\rangle} , \tag{3}$$

where C is the atomic concentration of pertinent defects, v_0 the atomic volume, $E^{\langle hkl\rangle}$ is the dynamic Young's modulus along $\langle hkl\rangle$, and T is the peak temperature. A parameter $\Psi^{\langle hkl\rangle}$ is given by the following equations for the $\langle 110\rangle$ split-type interstitials,

$$\Psi^{\langle 100\rangle} = 2(\tfrac{1}{2}\lambda_1 + \tfrac{1}{2}\lambda_2 - \lambda_3)^2 , \tag{4}$$

$$\Psi^{\langle 111\rangle} = (\lambda_1 - \lambda_2)^2 . \tag{5}$$

The λ_1, λ_2, and λ_3 are the principal values of the λ tensor for the elastic dipole of the defects. More generally, $\Psi^{\langle 110\rangle}$ can be given by

$$\Psi^{\langle 110\rangle} = \tfrac{1}{4}\Psi^{\langle 100\rangle} + \tfrac{3}{4}\Psi^{\langle 111\rangle} . \tag{6}$$

Because W is elastically isotropic, from Eq. (3):

$$\Psi^{\langle 110\rangle}/\Psi^{\langle 100\rangle} = \Delta_E^{\langle 110\rangle}/\Delta_E^{\langle 100\rangle} , \quad \Psi^{\langle 111\rangle}/\Psi^{\langle 100\rangle} = \Delta_E^{\langle 111\rangle}/\Delta_E^{\langle 100\rangle} . \tag{7}$$

Substituting the values of Eqs. (1) and (2) into Eq. (7), and applying the condition of Eq. (6), ratios can be determined for the 8-K peak,

$$\Psi^{\langle 110\rangle}/\Psi^{\langle 100\rangle} = 0.48 \pm 0.01 , \quad \Psi^{\langle 111\rangle}/\Psi^{\langle 100\rangle} = 0.31 \pm 0.01 , \tag{8}$$

and for the 27-K peak,

TABLE II. Properties of the main peaks in W and Mo.

	Peak temp.[a] (K)	Motional mode	Symmetry	$\frac{\lambda_1-\lambda_3}{\lambda_1-\lambda_2}$	Temp. of recovery (K)	Defects
W	8	rotation	$\langle 110\rangle$	1.8	~18	free interst.
	27	rotation	$\langle 110\rangle$	2.6	~30	trapped interst.[c]
Mo	12	rotation	$\langle 110\rangle$	2.5[b]	~28	free interst.
	39	rotation	$\langle 110\rangle$	2.5[b]	~42	trapped interst.[c]

[a] At ~500 Hz.
[b] Values corrected for numerical errors in Ref. 5.
[c] Trapped by other interstitial (i.e., di-interstitial) or by an impurity atom. Di-interstitial is more probable for W.

$$\Psi^{\langle 110\rangle}/\Psi^{\langle 100\rangle}=0.339\pm 0.001\ ,\qquad \Psi^{\langle 111\rangle}/\Psi^{\langle 100\rangle}=0.119\pm 0.002\ . \tag{9}$$

From these values and using Eqs. (4) and (5), one can obtain the anisotropy ratios of dipoles for the 8-K peak,

$$(\lambda_1-\lambda_3)/(\lambda_1-\lambda_2)=1.77\pm 0.02\ , \tag{10}$$

and for the 27-K peak,

$$(\lambda_1-\lambda_3)/(\lambda_1-\lambda_2)=2.55\pm 0.02\ . \tag{11}$$

If one knows the value of C in Eq. (3), the differences between the λ's can be estimated. The resistivity increase caused by 1 at.% Frenkel defects ($\Delta\rho_F$) is estimated by DiCarlo and Stanley[15] to be $\Delta\rho_F\approx 5\ \mu\Omega$ cm.[16] Using this value, from the resistivity measurements[12] the total concentration of Frenkel defects for the present 30-h irradiation is estimated as $C_t\approx 85$ ppm. For the neutron irradiation,[12] the percent recovery of the total induced resistivity $\Delta\rho/\Delta\rho_0$ is ~2.5% in stage I and ~4.5% in stage II_a. For the electron irradiation (Kunz *et al.*[17]) the $\Delta\rho/\Delta\rho_0$ is ~25% in stage I and ~13% in stage II_a.

In neutron irradiated specimens, many free interstitials would form clusters whose contribution to the resistivity might be not very small and thus, the amount of resistivity change in the stage-I recovery would not represent the concentration of free interstitials. Therefore, for the 8-K peak, C should be estimated from $\Delta\rho/\Delta\rho_0\approx 25\%$ observed in the electron irradiation, in spite of the fact that the present specimens were irradiated by neutrons. From the above consideration, for the 8-K peak, $C\approx 21$ ppm. Substituting this value into Eq. (3) and combining it with Eqs. (8) and (10), one obtains for the 8-K peak,

$$\lambda_1-\lambda_2=0.018\pm 0.001\ ,\quad \lambda_1-\lambda_3=0.032\pm 0.001\ . \tag{12}$$

For the 27-K peak (di-interstitial), there is no good criterion on which value of $\Delta\rho/\Delta\rho_0$ should be chosen to estimate C. A similar calculation as above with $\Delta\rho/\Delta\rho_0\approx 13\%$ gives

$$\lambda_1-\lambda_2\approx 0.046\pm 0.002 \text{ and } \lambda_1-\lambda_3\approx 0.118\pm 0.005\ ,$$

and with $\Delta\rho/\Delta\rho_0\approx 4.5\%$,

$$\lambda_1-\lambda_2\approx 0.079\pm 0.003 \text{ and } \lambda_1-\lambda_3\approx 0.201\pm 0.009\ .$$

Then, for the 27-K peak, one could say

$$\lambda_1-\lambda_2\approx 0.046\sim 0.079\ ,\quad \lambda_1-\lambda_3\approx 0.12\sim 0.20\ . \tag{13}$$

If the 27-K peak is associated with the rotation of the di-interstitials, Eq. (13) suggests that the configuration of the di-interstitials is such that the anisotropy of dipole is much more enhanced than single interstitials or that the axes of dipoles of two component single interstitials are parallel[18] but not perpendicular.[19] The results are summarized in Table II, together with the results on Mo.[5]

B. Peak at 30 K by DiCarlo *et al.*

DiCarlo *et al.*[3] found a peak at 30 K in electron irradiated W and studied it in great detail. At first sight, the present 27-K peak was considered to correspond with this peak, but it seems not so, after all, as shown below.[8] Let us compare the $\Delta_E^{\langle 100\rangle}$ of both peaks, based on the total resistivity increase $\Delta\rho_0$. They observed $\Delta_F^{\langle 100\rangle}\approx 17\times 10^{-5}$ for $\Delta\rho_0\approx 16.7$ nΩ cm after electron irradiation at 20 K. Corrected for the recovered amount of ~25% between 10~20 K (Kunz *et al.*[16]), $\Delta\rho_0\approx 22.3$ nΩ cm or, they should have obtained $\Delta_E^{\langle 100\rangle}/\Delta\rho_0\approx 7.6$ (mΩ cm)$^{-1}$ for irradiation at 10 K. In the present experiments, $\Delta_E^{\langle 100\rangle}\approx 32\times 10^{-5}$ for $\Delta\rho_0\approx 42.5$ nΩ cm, or $\Delta_E^{\langle 100\rangle}/\Delta\rho_0\approx 7.5$ (mΩ cm)$^{-1}$. The agreement between the two measurements seems to be very good. On the other hand, the values of $\Delta_E^{\langle 100\rangle}/\Delta_E^{\langle 100\rangle}$ are also not in disagreement in the error limit, but the values of $\Delta_E^{\langle 111\rangle}/\Delta_E^{\langle 100\rangle}$ are not reconcilable. Further, Arrhenius's plot in Fig. 9 suggests that the peak of DiCarlo *et al.* should correspond with the present 30-K peak.

In the present work, the 30-K peak appears half buried in the 27-K peak in the single-crystal specimens, but appears more pronounced in the impure polycrystalline specimen. Furthermore, although it is difficult to determine the peak height, the height seems to saturate at higher doses. Therefore, the defects of the 30-K peak are possibly associated with interstitials trapped by some impurity atoms (impurity-trapped interstitials).

Since DiCarlo *et al.* irradiated their specimens by electrons at 20 K where free interstitials were mobile, di-interstitial formation should have been scarce in their specimens. This could explain why they failed to find the large 27-K peak. As a matter of fact, a small peak at 27 K was noted by them. This gives support to the di-interstitial model for the 27-K peak.

C. Other minor peaks

After Seraphim and Nowick,[20] the orientation dependence of a relaxation strength of defects in cubic crystals can be given by

$$\Delta_E = \frac{\delta s_{11} - (2\delta s_{11} - 2\delta s_{12} - \delta s_{44})\Gamma}{s_{11}^U - (2s_{11}^U - 2s_{12}^U - s_{44}^U)\Gamma}\ , \qquad (14)$$

where s_{11}, s_{12}, and s_{44} are the usual elastic compliances, $\delta s_{11} = s_{11}^R - s_{11}^U$, s_{11}^R and s_{11}^U are the relaxed and unrelaxed elastic compliances, and similarly for s_{12} and s_{44}. The Γ is the orientation factor given by $\Gamma = \alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2$, where the α_i are the direction cosines between the cube axes and the stress direction $\langle hkl \rangle$. From Eq. (14), the Δ_E should vary monotonically with Γ and the extreme values of Δ_E must occur at the extreme orientations $\langle 100 \rangle$ and $\langle 111 \rangle$. In other words, a peak in the intermediate orientation must be intermediate in height between the $\langle 100 \rangle$ and $\langle 111 \rangle$. This rule applies quite generally to defects of any type in cubic crystals.

In the present case, if any relaxation peak appears larger in the polycrystalline or $\langle 110 \rangle$ specimens than in both $\langle 100 \rangle$ and $\langle 111 \rangle$ specimens, the origin of these peaks must be associated with impurities whose concentration is larger in the polycrystalline or $\langle 110 \rangle$ specimens. Conversely, if a peak is smaller in polycrystalline or $\langle 110 \rangle$ specimens than in both $\langle 100 \rangle$ and $\langle 111 \rangle$ specimens, the peak is considered to become arrested by impurities (for example, the 8- and 27-K peak in the polycrystalline specimen).

Thus, the origin of the peak at ~ 8 K, which appears transiently during annealing in the impure polycrystal, is considered to be an impurity trapped interstitial. The peak at ~ 10 K found by Townsend *et al.*[21] would also be of a similar origin. Similarly, the 34-, 60-, and 137-K peaks appear the largest in the polycrystalline specimen and are considered to be due to impurity trapped interstitials. For the 7-, 12-, 23-, 40-, and 50-K peaks, since no impurity effect was found and their heights

TABLE III. Properties of relaxation peaks in single-crystal W.

Peak. temp. (K)[a]	Height increases with dose	Defect symmetry	Possible defect type
7	...	...	interst. cluster
8	yes	⟨110⟩	free interst.
12	yes	⟨110⟩	interst. cluster
23	yes	?	interst. cluster
27	yes	⟨110⟩	di-interst.
30	...	⟨110⟩[b]	imp. trapped interst.
34	...	?	imp. trapped interst.
40	yes	⟨110⟩	interst. cluster
50	yes	⟨110⟩	interst. cluster
60	...	?	imp. trapped interst.
137	...	?	imp. trapped interst.

[a]At ~ 500 Hz. [b]From DiCarlo *et al.* (Ref. 3).

increase with dose, they could be assigned to interstitial clusters of various sizes, but the possibility of impurity trapped interstitials can not completely be denied. These results are summarized in Table III. Among these peaks, the 23-, 34-, and 40-K peaks are also observed by DiCarlo *et al.*[3,22] Besides these peaks, all the peaks observed at around 14, 54, 74, 82, and 97 K in the polycrystalline specimen are also considered to be due to impurity trapped interstitials. Identification of these kinds of impurities is not possible at present.

D. Low-temperature recovery

From the quench experiments, the activation energy for the migration of vacancies is given as ~ 1.8 eV.[23] Therefore, in the present experiments the whole recovery is associated with defects of interstitial types and the recovery stage of free interstitials is of primary interest. As it was discussed previously,[2,8] the free migration of interstitials occurs at stage I (~ 18 K) and their stress-induced rotation produces the 8-K peak.

The next large recovery stage in resistivity measurements, i.e., stage II_a (~ 30 K) is proposed to be due to the recovery of di-interstitials in the present experiments. Looking for the recovery spectra of resistivity, one finds that the stage-II_a recovery appears larger in the results of Kunz *et al.*[17] than those of Coltman *et al.*[24] Since Kunz *et al.* used electron irradiation and Coltman *et al.* irradiated by thermal neutrons, a distribution of Frenkel defects should have been uniform in both irradiations and the probability of di-interstitial formation could be compared. Their results are reasonable for the di-interstitial model because $\Delta\rho_0$ is about nine times larger in the former than in the latter. On the other hand, if one examines an analogy between W and Mo (see Table II), the recovery stage of Mo at ~ 42 K which seems to correspond with stage II_a of W, always appears larger than the recovery stage at ~ 28 K which corresponds to stage I of W.[5] The origin of this difference is not known at present (see Ref. 25 for further discussion).

The recovery curves of the two peaks shown in Fig. 5 are obviously too broad in temperature to be explained if the defects were distributed uniformly. This broad recovery is considered to be due to the localized distribution of the defects in fast-neutron irradiation.

The other recovery stages [II_b (~ 40 K), II_c (~ 60 K), and II_d (~ 80 K)], seem to correspond, respectively, with the recoveries of the 40-, 12-, and 50-K peaks, which are possibly due to interstitial clusters of various sizes. If so, these stages are intrinsic, but not related to impurities. Further evidence would, however, be required to specify their origins. The 34- and 137-K peaks which are apparently due to impurity-trapped interstitials, anneal out at around 200 K and this is just the stage which appears large only in the resistivity measurements of impure specimens.[12]

V. CONCLUSIONS

In the internal-friction and dynamic-modulus measurements on W single-crystals and polycrystal after fast-neutron irradiation near liquid-helium temperature, two pronounced relaxation peaks at 8 and 27 K (~ 500 Hz) were observed. From the measurements of their recovery, dose dependence, orientation dependence, peak shift, and impurity effect, it is suggested that the origin of these peaks are the stress-induced rotation of the ⟨110⟩ split self-interstitials of two different types and these interstitials are the defects of stage I (~ 18 K) and II_a (~ 30 K), respectively. Further, the defects of the 8-K peak are suggested to be free interstitials and those of 27-K peak, probably to be di-interstitials. The peak found by DiCarlo *et al.* at 30 K (~ 600 Hz) is suggested to be due to interstitials trapped by impurity atoms. Using a rule of orientation dependence, the other minor peaks are attributed to either interstitials trapped by impurity atoms or probable interstitial clusters. A comparison of their recovery temperatures with the resistivity recovery stages seems to reveal the intrinsic recovery stages. To definitely identify these intrinsic stages, however, experiments on higher irradiation doses would be required. The present work exemplifies the importance of internal-friction techniques to study the point defects in bcc metals.

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