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I. INTRODUCTION

It has been established(1-5) that there exists a strong connection between the appearance of thermally activated peaks in the curves of internal friction versus temperature, otherwise known as "Bordoni peaks," and the occurrence of plastic flow in a number of fcc metals. The defects responsible for this mechanical relaxation phenomenon are probably connected with (1) the dislocations associated with the plastic flow and/or (2) the point defects produced during the plastic flow. The available evidence indicates that the thermally activated motion of dislocation lines is the source of the relaxation.

Several models of thermally activated dislocation motion have been recently advanced(6-11) that may provide a basis for explaining these peaks. One of the essential features of these models is the existence of energy barriers to the motion of some segment of the dislocation line; the heights of these barriers are characteristic of a given metal and are not necessarily dependent on the presence of impurities. At low temperatures the movement of the dislocation through the lattice in response to a small externally applied stress is then controlled by the thermally activated motion of the dislocation segments over the energy barriers. The size and distribution of these energy barriers are thus characteristic of the mechanical state of a given pure metal and should be considered among the important parameters that determine the plastic properties of that metal.

In contrast to the growing literature on the Bordoni and subsidiary peaks in copper,(12-15) aluminum,(16, 17, 18) and other fcc metals, very little information is available concerning even the existence of analogous mechanical relaxation peaks (which are collectively called "deformation peaks" in this paper) in other metals.(19)

Early work(20) by the present authors showed the existence of a thermally activated internal-friction peak in plastically deformed niobium.

This peak had an activation energy of no greater than 0.3 ev and a relaxation strength (peak height) that depended on prior amounts of plastic deformation. It was also shown that the peak disappeared with a relatively low-temperature heat treatment that also produced a greater than fiftyfold increase in the oscillation-strain amplitude necessary to produce strain-dependent internal friction and modulus (breakaway strain). This low-temperature annealing was attributed to the pinning of the dislocation relaxation oscillators by interstitial impurities that had diffused to the dislocation lines during the anneal. It was not established at that time whether the observed activation process was attributable to an intrinsic dislocation interaction with the lattice or to a thermally activated jumping of an impurity atom bound in the stress field of the dislocation line.

Later work(21) has shown that similar peaks exist in cold-worked tantalum, molybdenum, and tungsten. These peaks also anneal at relatively low temperatures and show a marked increase in the breakaway strain following the anneal. It was concluded in Ref. 21 that the peaks observed in the refractory bcc metals are probably of an origin similar to that of the Bordoni peaks in copper.

The present paper expands these earlier studies to include measurements of the activation energies and of attempt frequencies of most of the peaks by making measurements on the same specimens from 5 to 100,000 cps. The dependence of the heights and temperatures of the peaks on the amount of prior deformation is examined in some detail for molybdenum, niobium, and very pure tantalum over an extended range of deformation. Use is also made of the low-temperature annealing phenomena seen in earlier work to measure the modulus defect as a function of temperature in molybdenum. Finally, the role that impurities play in determining the structure of the deformation peaks is demonstrated by results of a study of zone-refined and ultra-high-vacuum degassed specimens of molybdenum and tantalum.

II. PREPARATION AND ANALYSIS OF SPECIMENS

Most of the specimens used in this investigation were in the form of 4- to 5-in.-long bars that were 0.125 in. in diameter. They were vacuum-annealed ($\sim 10^{-5}$ mm Hg) for several hours at $\sim 1100^{\circ}$C and then furnace-cooled to room temperature before being subjected to the various regimes of cold working and thermal aging. Such treatment generally produced specimens of moderate grain size (~ 50 to 100 μ). Specimen Nb-13 received a special heat treatment designed to coarsen its grain structure. The treatment of this specimen consisted of resistance heating to 1800°C for 4 hr in a cold-trapped vacuum system producing a vacuum of 2×10^{-6} mm Hg. The resulting grain size was generally equal to or larger than the diameter of the specimen.

Specimen Mo-Z was zone-refined by an electron-beam floating-zone process in a vacuum of $\sim 1 \times 10^{-5}$ mm Hg. Three zone passes were made at an average traverse velocity of 0.10 in./min. The resulting rod was composed of about three single crystals. The starting material was electron-beam-melted molybdenum obtained from the Stauffer-Temescal Company. Specimen Ta-6 was decarburized by resistance heating to a temperature of $\sim 2300^{\circ}$C for 6-1/2 hr in the presence of 5×10^{-5} mm Hg of oxygen. It was then degassed by heating it to $\sim 2800^{\circ}$C(22) for 10 min in a vacuum of 2×10^{-9} mm Hg. The specimen starting material was National Research Corporation, 40-mil-diameter tantalum wire obtained through the courtesy of D. P. Seraphim of International Business Machines Corporation. The average diameter of the wire following the refining process was 36.5 mils. Typical "bamboo" structure resulted from the treatment, the average grain length being about three times the grain (specimen) diameter.

Individual gas analyses and several carbon analyses were made on the specimens and the results are given in Table 1. The ratio, Γ, of the room-temperature electrical resistance to the resistance at $\sim 5^{\circ}$K was measured for a number of the specimens; these results are also given in Table 1.

Table 1

ANALYSIS OF SPECIMENS

Specimen No.	Interstitial Impurities (wt ppm)				Total Metallic Elements (wt ppm)	$\Gamma = \frac{R\ 300^{o}K}{R\ 5^{o}K}$
	Carbon	Nitrogen	Oxygen	Hydrogen		
Nb-3	--	60	130	30	3000	-----
Nb-10	--	100	130	25	3000	-----
Nb-11	--	70	140	30	----	-----
Nb-13	--	100	150	1	----	-----
Ta-2	--	80	50	10	----	-----
Ta-4	20	90	50	10	----	88
Ta-6	--	---	---	--	< 100	1000 to 1200
Ta-8	(*)	(*)	(*)	(*)	< 260	7.29
Ta-A	60	70	70	5	----	-----
Mo-3	--	80	150	1	----	56.7
Mo-4	20	40	170	6	----	-----
Mo-A	--	5	20	0.7	----	70
Mo-Z	--	2	5	0.7	----	120
W-1	--	10	95	4	----	25

*Total interstitial impurities < 100.

III. METHOD OF MEASUREMENT

Measurements of the internal friction, Q^{-1}, and of Young's dynamic modulus were made in the kilocycle frequency range by the resonant-bar method using needle-nodal supports. Electromagnetic drive-and-pickup transducers were used to excite and detect the oscillation of the specimen. The frequency was varied by selecting from the odd longitudinal vibration modes. A relatively wide range of oscillating-strain amplitudes could be obtained ($\sim 5 \times 10^{-8}$ to 5×10^{-4}) because of the relatively strong coupling between the driver and the 0.006-in.-thick ferromagnetic disks that were spot-welded to the ends of the specimens. The Q^{-1} of the specimen was determined by measuring the half-power point of the resonance curve. The background Q^{-1} was less than 1×10^{-5}.

Measurements of the Q^{-1} and the rigidity modulus were made in the 0.5- to 80-cps range in the torsional oscillation mode by the use of an sensitive, inverted torsion pendulum.(23) This instrument has a very low instrumental background damping (less than 2×10^{-5}) and is able to measure Q^{-1} and the period of oscillation at surface strains as low as 5×10^{-8} by means of a sensitive double-photocell readout system.(24)

In both the kilocycle-range apparatus and the inverted torsion pendulum the temperature of the specimen was controlled by means of a furnace winding surrounding the specimen space. The region outside the furnace was maintained either at liquid-nitrogen, at subliming-nitrogen, or at liquid-helium temperatures by means of a double-glass Dewar system that enclosed the furnace volume. The temperature was maintained sensibly free of gradients by means of a low-pressure (300 μ) of helium exchange gas and was monitored by means of three copper-constantan thermocouples that were placed near, but not touching, the specimen. Care was taken to ascertain the error incurred by preventing the thermocouples from touching the oscillating specimen. This error seldom exceeded 0.2°C under standard heating conditions. A constant temperature could be maintained during a measurement by balancing the heat input from the heaters against the heat lost to the bath, or the temperature could be allowed to increase slowly. The allowable rate of rise of the temperature was governed by the temperature difference established between the thermocouples. The temperature gradient was never allowed to exceed 1°C/ft during a standard test.

Since the low-frequency components of the vibrations from the boiling of the liquid coolants coupled strongly into the torsion pendulum, provision was made to freeze the liquid-nitrogen bath by mechanical pumping. The pumping line was low-frequency filtered by a massive concrete terminal block.

IV. EXPERIMENTAL RESULTS

Frequency Dependence

The internal friction of prestrained polycrystalline molybdenum is plotted as a function of temperature in Fig. 1. These measurements were made on specimen Mo-3 in a torsional vibration mode near 5 cps and in the fundamental longitudinal mode near 28, 000 cps. The two broad peaks in Fig. 1 (the low-temperature peak will be referred to as the α peak and the high-temperature peak as the β peak) in molybdenum are also representative of the low-frequency spectrum of both prestrained niobium and tantalum. Under some conditions, to be considered later, both the α and the β peaks can be resolved into several component peaks that will be designated by suitable subscripts. For example the β peak in molybdenum shown in Fig. 1 has at least two components, β_1 and β_2. It is also evident in this figure that both the α and the β peaks are shifted to lower temperatures when measurements are made at lower frequencies.

Figure 2 shows the temperature shift with change in frequency for the α peak in specimen Nb-10, measured at a strain amplitude, ϵ_m, of 10^{-7}. The rapid increase in the internal friction on the high-temperature side of the 8-cps curve is the beginning of the β peak; the β peak lies above 300°K for the kilocycle measurements. The most extensive measurement of the shift of the temperature of these internal-friction peaks with change in measurement frequency has been made in niobium. In Fig. 3 the data for niobium obtained in this investigation are plotted as the logarithm of the frequency, f, of measurement versus the reciprocal of the peak temperature, T_P, in an attempt to determine whether the peaks are governed by a simple thermally activated process obeying the relation $f = f_0 \exp(-H/R\, T_P)$, where f_0 is the frequency of the process at infinite temperature (i. e. , the attempt frequency) and H is the activation energy of the process. Included in this plot are the data of Bruner(13) and DeBatist.(25) Recent data reported by Bordoni(26) were not available at the time of writing. It can be seen that

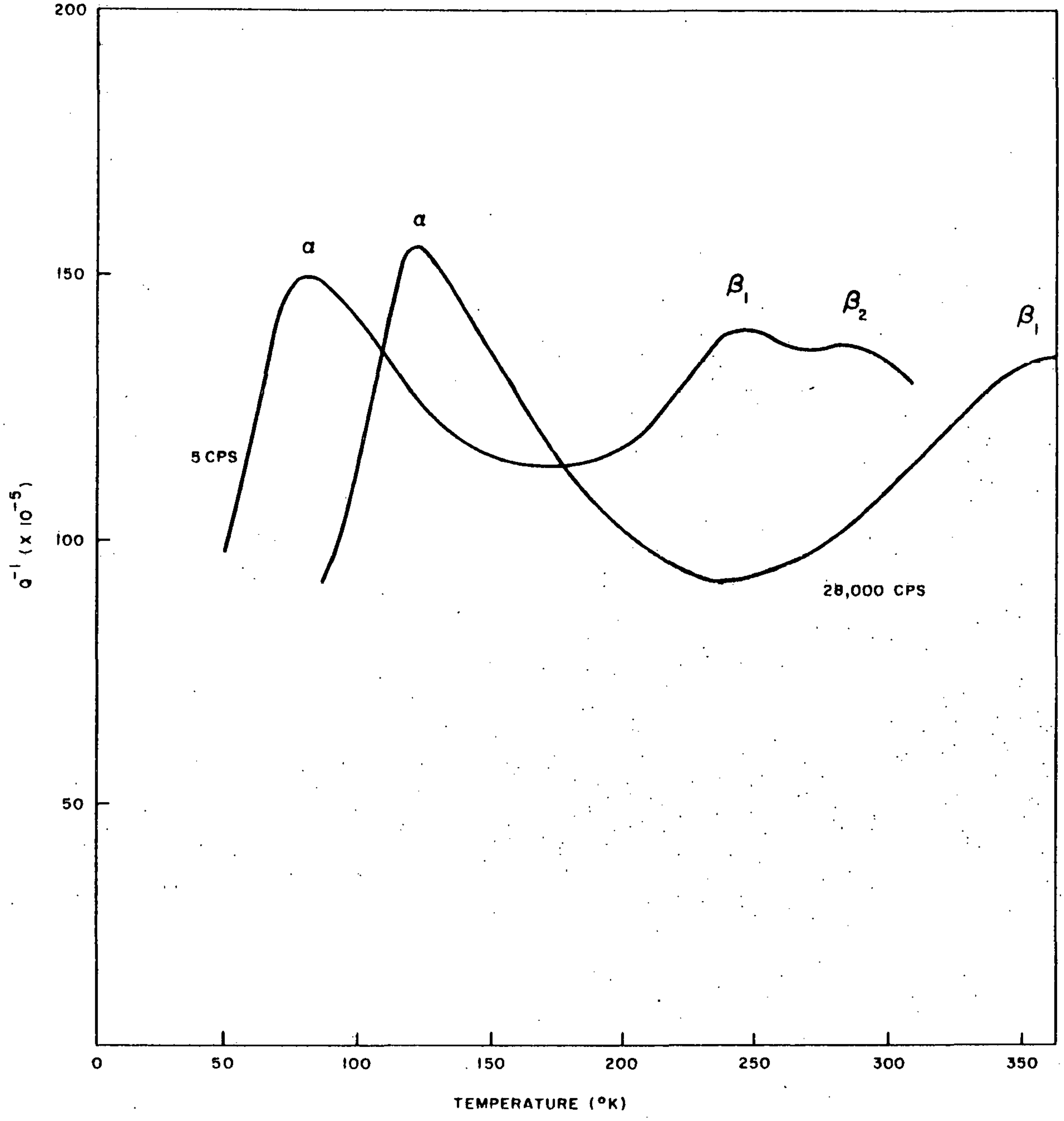

Fig. 1--Temperature dependence of the internal friction in polycrystalline Mo prestrained 5% in tension; measurements at 5 cps were made in the torsional mode at surface strain amplitude of 2×10^{-7}; measurements at 28,000 cps were made in the fundamental longitudinal mode at a strain amplitude of $\sim 10^{-7}$

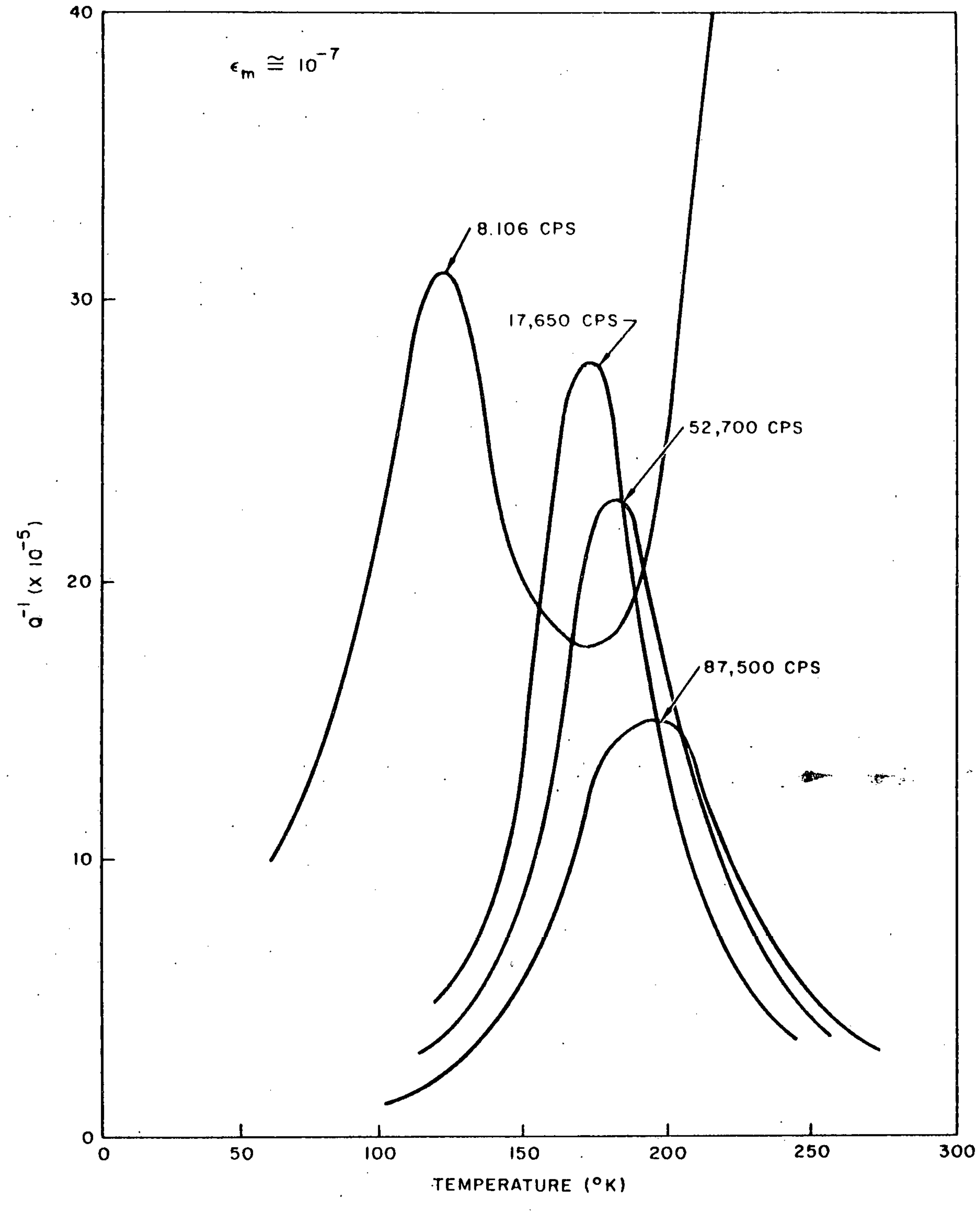

Fig. 2--Temperature dependence of the internal friction in polycrystalline Nb-10 prestrained 5% in tension; measurements at 8 cps were made in the torsional mode at a surface strain amplitude of 1×10^{-7}; all other measurements were made at the fundamental and odd-harmonic longitudinal modes at a strain amplitude of $\sim 10^{-7}$

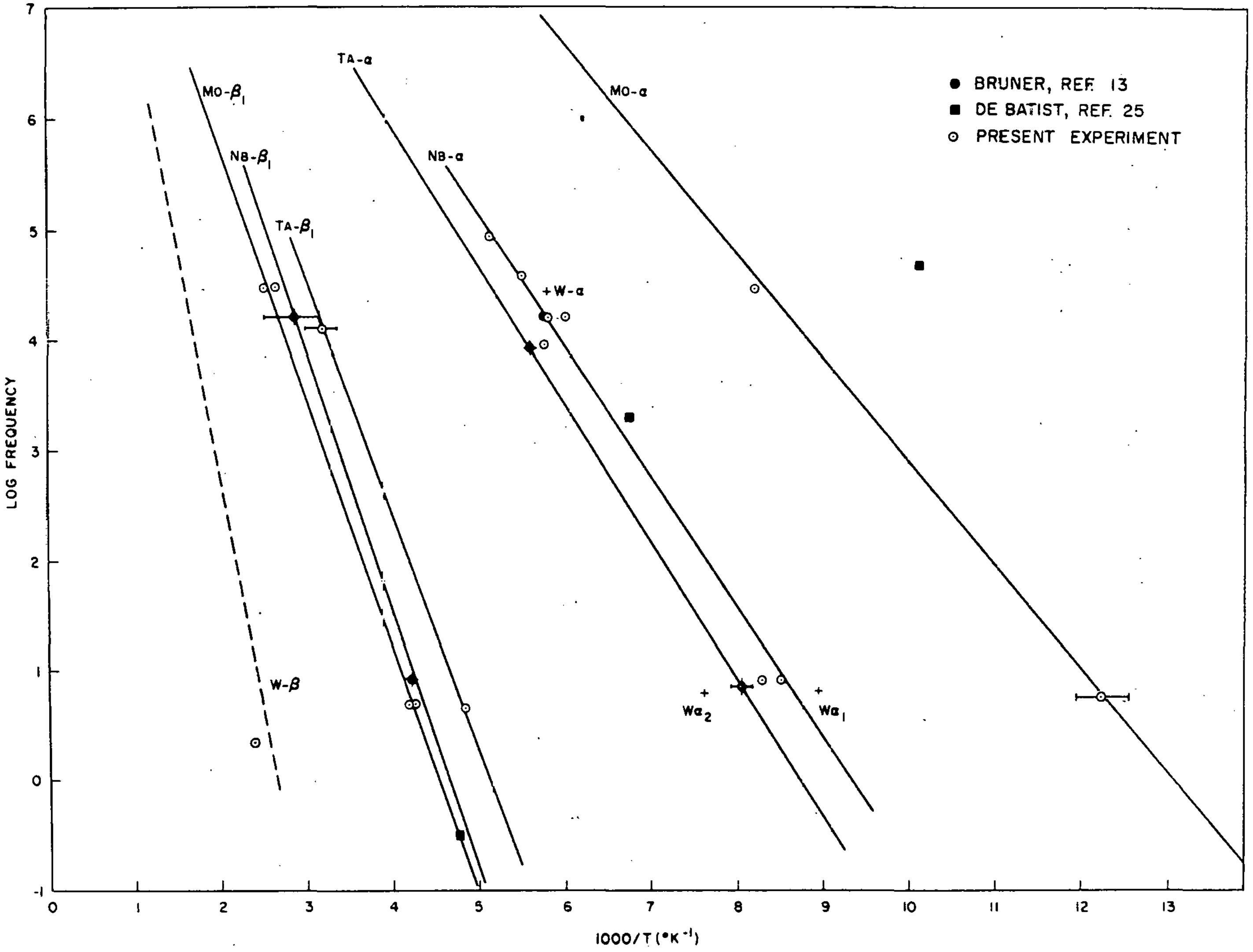

Fig. 3--Arrhenius plots of the temperature at which various internal-friction peaks occur versus the frequency of measurement

the data appear to lie on a straight line which gives an activation energy H of 0.24 ev and a value of 1.3×10^{11} $\sec^{-1}$ for the attempt frequency f_0. The kilocycle measurements of the relatively pure, large-grained specimen Nb-13 lie below the straight line. Either a large component of postrelaxation background internal friction could shift the peak temperature upward in specimen Nb-13, or the impurity effect may be responsible for this displacement. Both the postrelaxation internal-friction background and the impurity effect will be discussed later.

Along with the data for niobium in Fig. 3, the relatively limited results obtained on the α peaks of molybdenum, tantalum, and tungsten are included.

Included in the plot of Fig. 3 is the one point on molybdenum from the work of DeBatist.(25) Since both of the points on molybdenum from the present investigation were obtained on the same specimen, it was decided to derive the activation energy and attempt frequency for the α peak of molybdenum from only these two points. The large discrepancy between DeBatist's measurement and those of the present investigation will be considered in the section on the effect of impurities on the peak structure.

Essentially, the temperature-shift data for tungsten are only qualitative, since one specimen was used to make the kilocycle measurements while another one was used to make the low-frequency measurements; therefore, only broad limits can be placed on the estimate of the activation energy and attempt frequency.

Also included in Fig. 3 are the few available data concerning the temperature shift with frequency of the β peaks. Since the β peaks generally are easily resolved into several separate peaks, the lowest temperature (or β_1) peak of the group is that which is measured as a function of frequency. The most reliable β-peak data are those for molybdenum and tantalum; some information is known concerning niobium, but a limit can be set on the activation energy of tungsten only by assuming a value of the attempt frequency based on information for molybdenum. The results of the measurements and estimations shown on Fig. 3 are summarized in Table 2; for comparison, two fcc metals, aluminum and copper, are included.

Table 2

ACTIVATION ENERGIES AND ATTEMPT FREQUENCIES

	α Peaks		β Peaks	
Element	$f_0(\mathrm{sec}^{-1})$	H(ev)	$f_0(\mathrm{sec}^{-1})$	H(ev)
Nb	1.3×10^{11}	0.24	1×10^{11}	0.47
	1.6×10^{11}[a]	0.23[a]		
	9.7×10^{11}[b]	0.265[b]		
Mo	8×10^{11}	0.18	2.6×10^{10}	0.46
Ta	1×10^{11}	0.25	1×10^{11}	0.43
W	-----	0.24[c]	-----	>0.6
	$\sim10^{11}$	$\sim$0.25		
Element	Subsidiary Peaks		Bordoni Peaks	
Cu	9.5×10^{8}[d]	0.041[d]	4×10^{11}[d]	0.122[d]
	3.2×10^{11}[e]	0.05[e]	1.5×10^{11}[e]	0.113[e]
			4×10^{12}[f]	0.14[f]
Al	1×10^{10}[g]	0.024[g]	-----	0.11[h,i]

[a] R. E. DeBatist, Ref. 25.
[b] P. G. Bordoni, M. Nuovo, and L. Verdini, Ref. 26.
[c] D. R. Muss and J. R. Townsend, Ref. 27.
[d] P. G. Bordoni, M. Nuovo, and L. Verdini, Ref. 12.
[e] G. A. Alers and D. O. Thompson, Ref. 14.
[f] D. H. Niblett, Ref. 15.
[g] E. Lax and D. H. Filson, Ref. 18.
[h] T. S. Hutchison and A. J. Filmer, Ref. 16.
[i] N. G. Einspruch and R. Truell, Ref. 17.

The β peaks of niobium and tantalum are usually difficult to observe in the kilocycle frequency range, since the peaks appear at temperatures where they are unstable. This instability is part of a relatively low-temperature annealing phenomenon that was observed earlier in niobium(20) and molybdenum.(21) Such relatively low-temperature annealing has not been reported for the fcc metals, and thus they must be considered a distinguishing feature of the deformation peaks in the bcc transition metals. This phenomenon will be considered in more detail in the section on thermal aging.

The appearance of resolvable peak components in the β peak of molybdenum leaves little doubt that it is really a group of peaks. The structure of the α peak, however, is less obvious. That the α peaks in all metals studied so far are several times wider than a simple relaxation process is shown in Fig. 4, on which are plotted the reciprocal half-widths of the various α peaks versus the reciprocal peak temperature, T_P. T_L is the temperature at which the peak falls to half of its maximum value on the low-temperature side.

In such a plot, a collection of simple thermally activated relaxation processes that have a single activation energy but have a distribution of attempt frequencies will maintain its reciprocal temperature width as the frequency is lowered and, therefore, as $1/T_P$ is raised. It is seen in Fig. 4 that the width, in fact, increases with decreasing peak temperature, hence ruling out the possibility of a single activation energy for the α peak. This leaves the alternative of having either several relaxation processes, all with the same attempt frequency but a distribution of energies, or a distribution of both frequencies and energies. Since the former possibility is consistent with the observations and the simpler of the two, it is assumed for simplicity that the α peaks are composed of several subpeaks all having the same attempt frequency but with a distribution of activation energies. From Fig. 4 it is also apparent on the basis of the widths of the α peaks alone that niobium and tantalum should be classed together, while molybdenum and tungsten belong in another class with considerably broader peaks. More will be said concerning this observation later.

Prestrain Dependence

The curves in Fig. 5 show the internal friction versus temperature for "single-crystal" specimen Nb-13 plotted as a function of various amounts

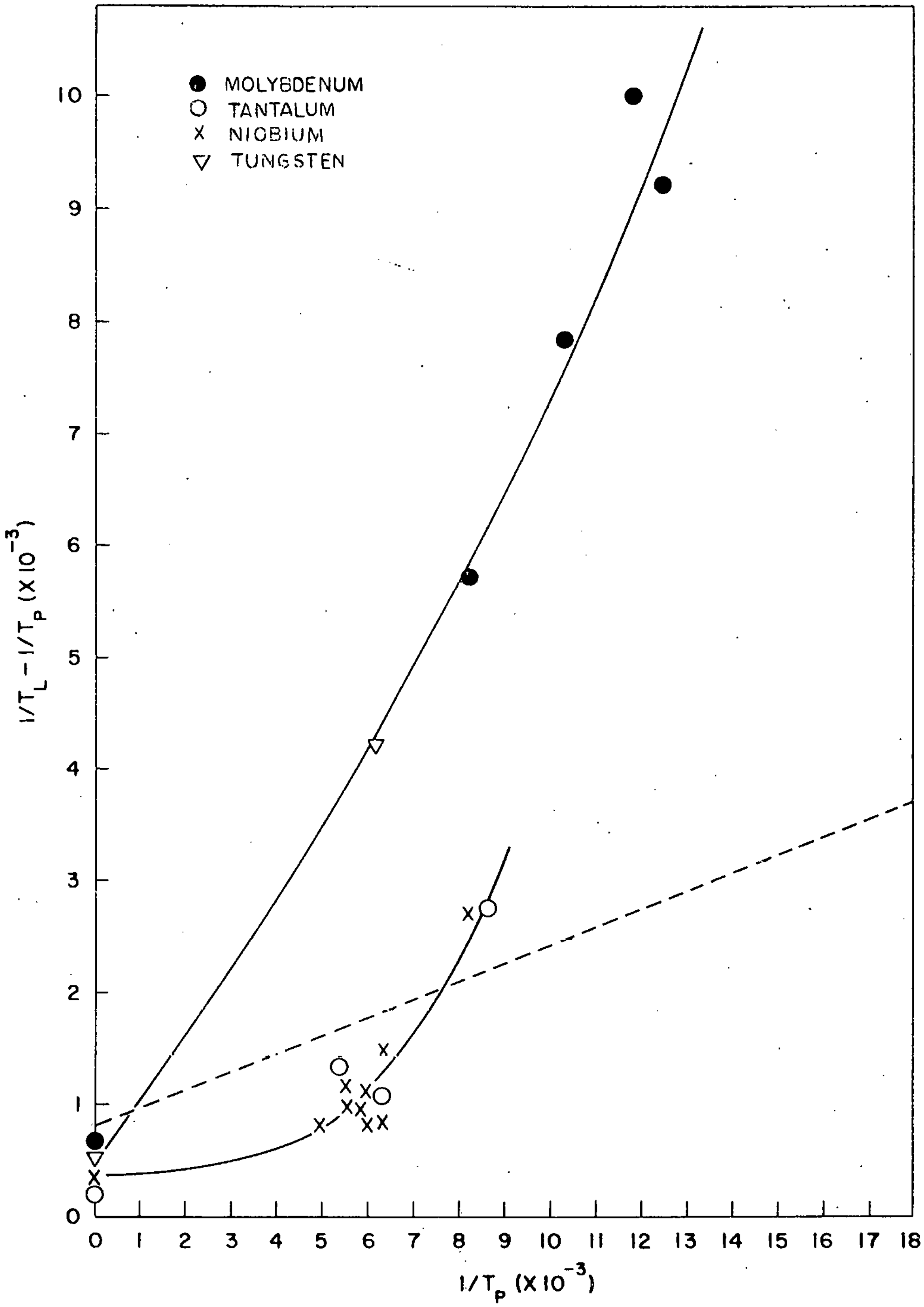

Fig. 4--The dependence of the width of the low-temperature half of the α peak in Ta, Nb, Mo, and W on the peak temperature, T_P; T_L is the lower temperature at which the internal friction due to the relaxation peak has decreased to half its maximum value; the dashed line corresponds to Niblett's evaluation (Ref. 15) of the Bordoni-peak data for Cu

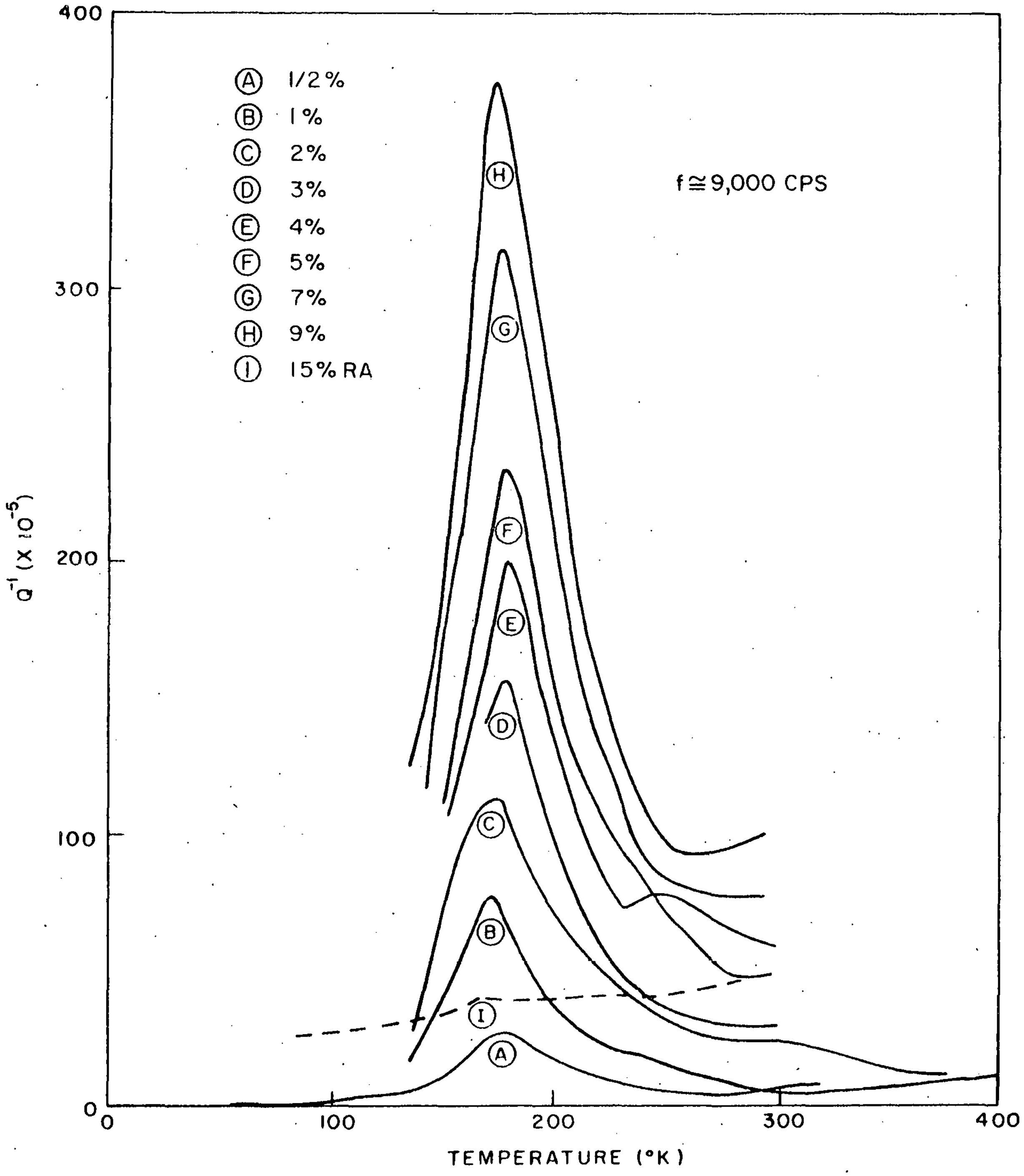

Fig. 5--The dependence of the internal-friction spectrum of the α peak in "single crystal" Nb-13 on the amount of prior plastic deformation; measurements were made at 9, 300 cps in the fundamental longitudinal mode at a strain amplitude of $\sim 10^{-7}$; the amount of prior tensile deformation at room temperature is shown on the legend for each curve

of tensile prestrain. The specimen was pulled successively in tension and measured after each extension. Necking in the large grains prevented exceeding 10% by tensile deformation. The specimen was cold-worked beyond 10% by a reduction in area of about 15%. Notice that the α peak increases in height monotonically up to ~10% and decreases for greater prestrains. Earlier work(20) in less-pure polycrystalline niobium showed a maximum internal friction for the α peak with about 3% prestrain. These measurements were in the kilocycle range and show only the α peak for the reasons mentioned previously. Measurements in the torsional mode made at 7.8 cps show the behavior of both the α and the β peaks for a 5% prestrain in tension and also for ~5% additional strain applied by twisting. The results are shown in Fig. 6. Both peaks rise with increasing amounts of prestrain, the α peak rising faster than the β peak. The prestrain dependence of tantalum is similar to that found in niobium.

Figure 7 shows the prestrain dependence of specimen Mo-4 measured at 15,000 cps and strained small amounts from ~0.1% up to ~1%. Notice the general increase in both the α- and β-peak heights and the change in the shape of the α peak from a flat-topped peak that extends from 80° up to 92°K for the 0.1% deformation, to a relatively sharp peak centered near 115°K for the 1.1% deformation. The temperature of the center of the peak shifts from about 90° to 115°K. For deformations up to 12% the peak position shifts further up to about 120°K.

For more extensive amounts of deformation these measurement were extended by twisting specimen Mo-4 up to 80% surface strain. The results of these measurements are plotted in Fig. 8. For this particular specimen purity and grain size, it is seen that the α peak reaches a maximum of 300×10^{-5} at about 15% strain, and the β peak reaches a maximum of 150×10^{-5} for strains of ~20%. Thereafter, both peaks descend with increasing amounts of prestrain. At about 80% prestrain the specimen fractured at the grips.

The limited measurements of tungsten prestrained to about 1% and 3%

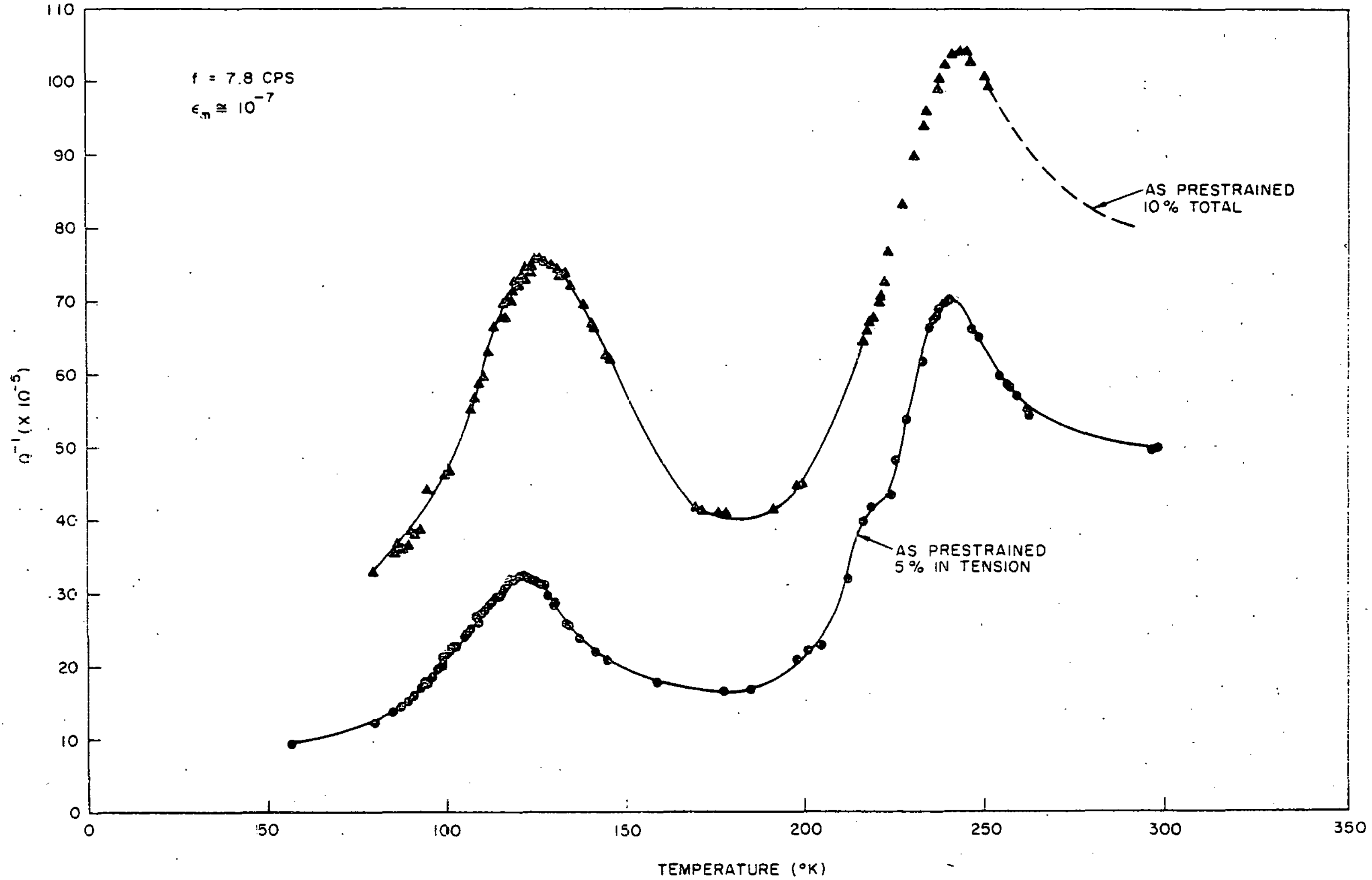

Fig. 6--Temperature dependence of the internal friction in polycrystalline Nb prestrained at room temperature 5% in tension and 5% in torsion; the measurements were made in the torsional mode at 7.8 cps at a surface strain amplitude of 2×10^{-7}

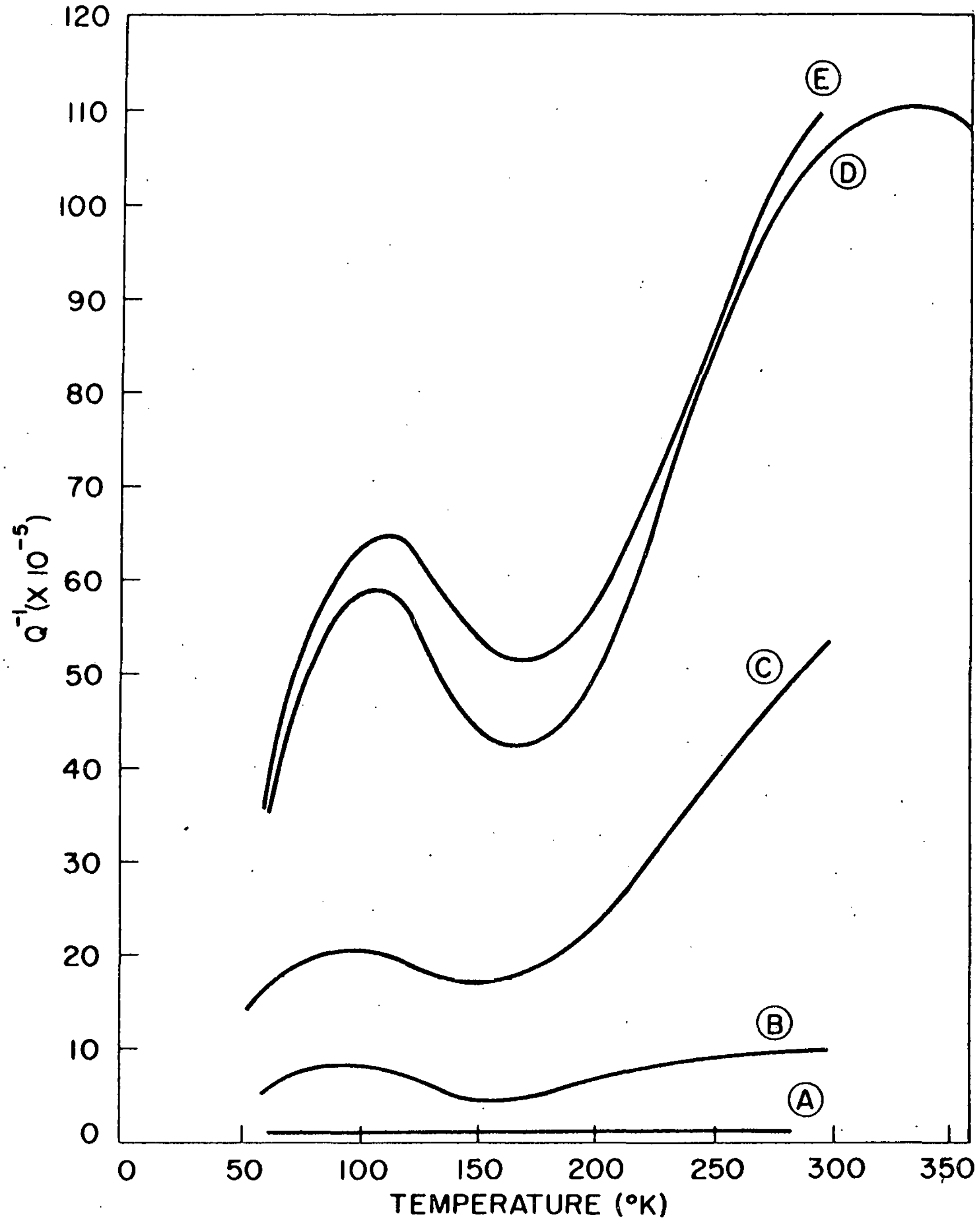

Fig. 7--The dependence of the internal-friction spectrum of polycrystalline Mo on the amount of prior deformation at room temperature; frequency of measurement was 15,000 cps; (A) as annealed for 3 hr at 1100°C, (B) as deformed 0.1%, (C) as deformed 0.3%, (D) as deformed 0.9%, and (E) as deformed 1.1%

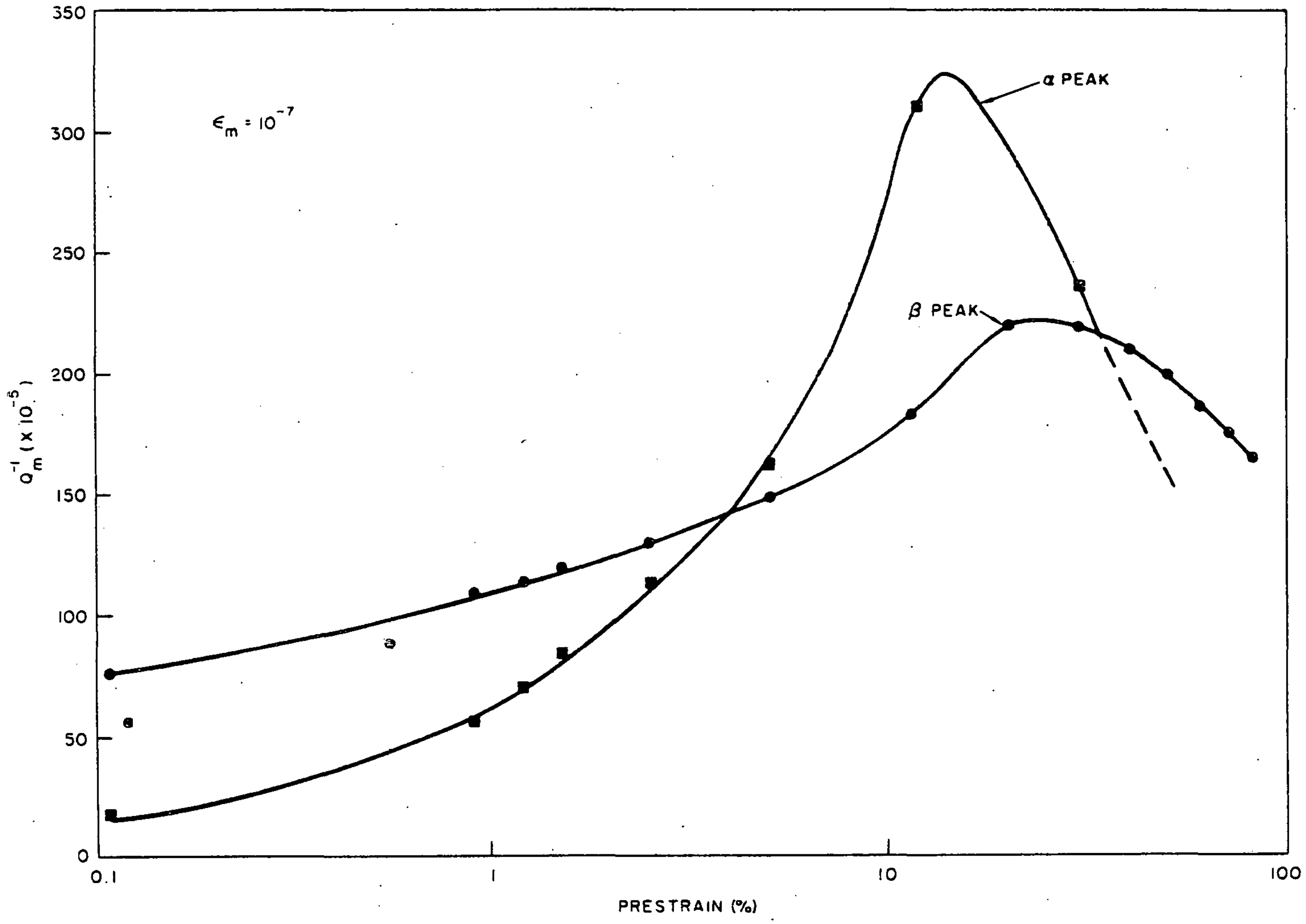

Fig. 8--The dependence of the height of the α and β internal-friction relaxation peaks in polycrystalline Mo on the amount of prior room temperature deformation; measurements were made near 20,000 cps at a strain amplitude of ~10^{-7}

at 400°C are shown in Fig. 9. It appears that the prestrain dependence of this metal resembles that of the others, at least for small amounts of prestrain.

Effect of Thermal Aging

Earlier kilocycle-level work with niobium(20) showed that what we now call the α peak is removed by a relatively low-temperature heat treatment of 210°C for 25 min. It was also pointed out in Ref. 20 that accompanying the disappearance of the peak was approximately a fiftyfold increase in the breakaway amplitude (the oscillating strain at which the specimen showed amplitude dependence in the internal friction and modulus).

Aging effects in the internal-friction spectrum of prestrained molybdenum have also been reported before.(21)(25) It was noted in Ref. 21 that aging for 1 hr at 300°C produced evidence of multiple peaks in the β peak. The α peak was shifted downward in temperature and showed some evidence of structure. These aging effects were interpreted as being due to the pinning of dislocation lines by impurities that have diffused to them during the aging treatment.

Figure 10 shows the effect of thermal aging of specimen Ta-2 for 1 hr at 200°C. The peak at 184°K was reduced in height to about one quarter of its former value, and the peak temperature was shifted downward to 165°K. These peak modifications were accompanied by an approximately threefold increase in the breakaway strain amplitude. Re-straining produced the peak once more at ~183°K.

Figure 11 shows the effect of successive isochronal aging treatments (the aging time was 1 hr) on the temperature dependence of both the internal friction and resonance frequency of specimen Mo-3. Since the frequency, f, and the Young's modulus, M, are connected by the relation $4\ell^2 f^2 = M/\rho$ when a thin bar of length ℓ and density ρ is resonating in the fundamental longitudinal mode, and since the temperature dependence of the elastic component of the modulus is so much stronger than the dimensional changes, one can consider that fractional-frequency changes, $2\Delta f/f$, are equal to

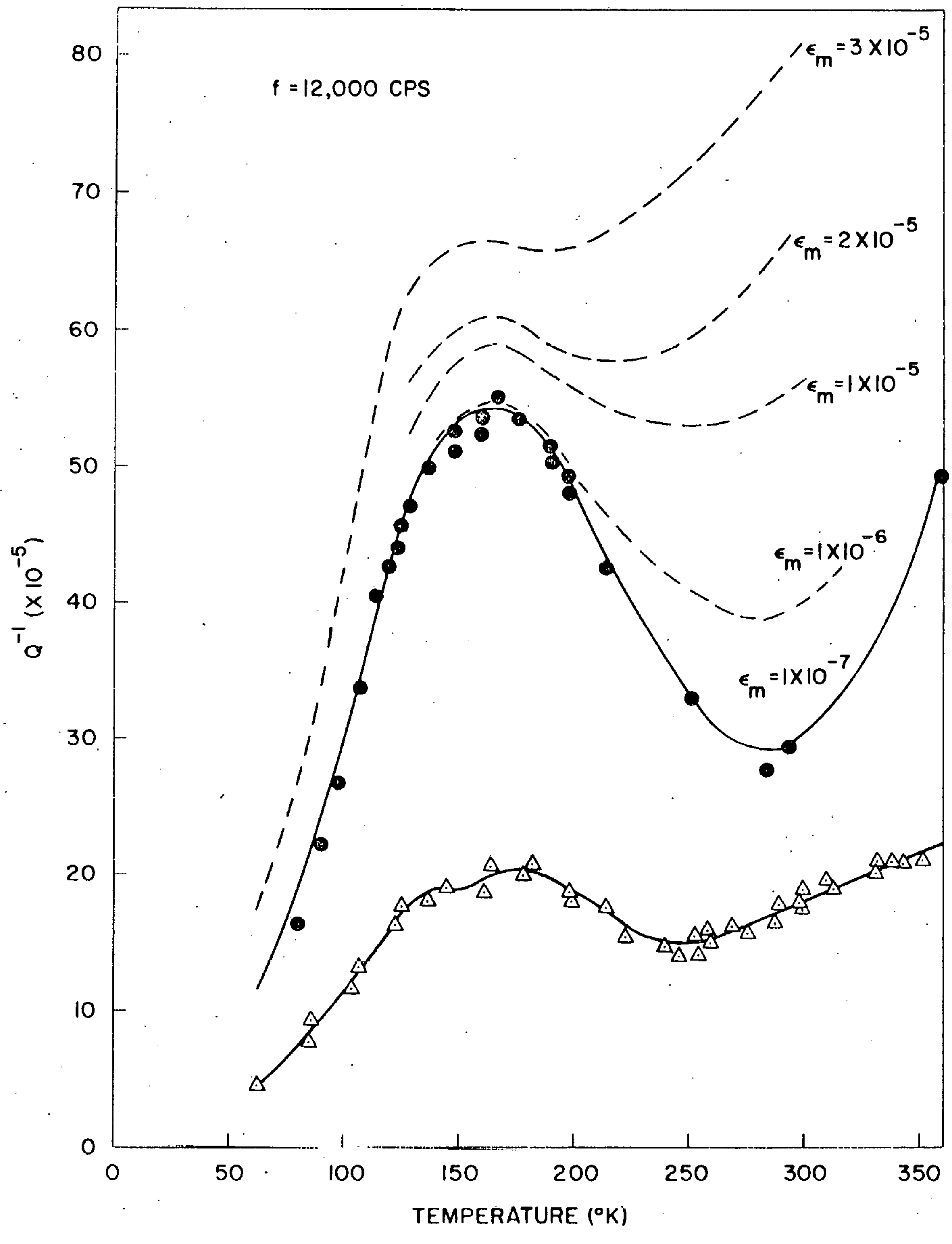

Fig. 9--The dependence of the internal-friction spectrum of polycrystalline W on amount of torsional prestrain at 400°C and oscillating strain amplitude; frequency of measurement was 12,000 cps; lower curve was prestrained ~1% and upper curve, ~3%

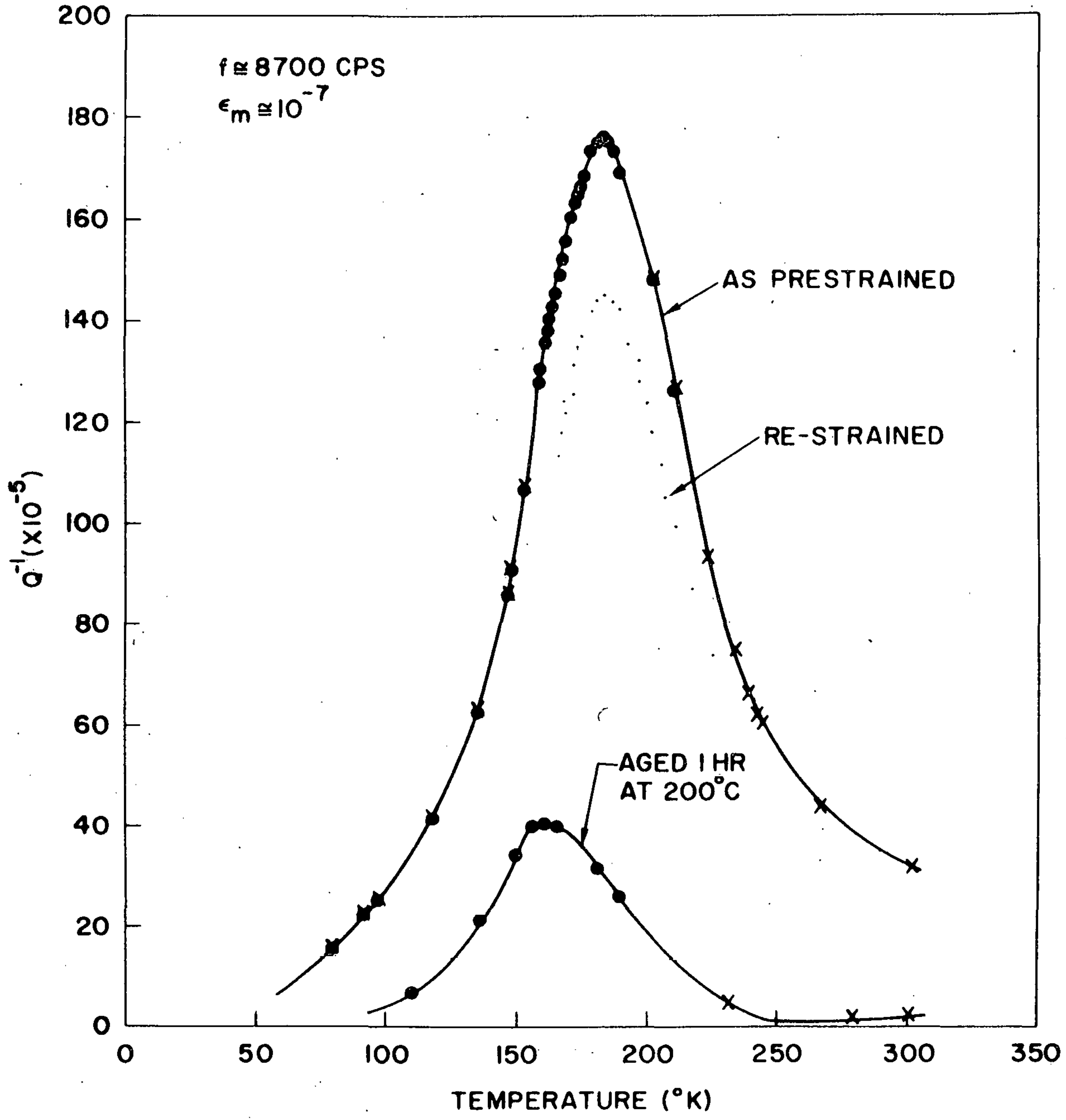

Fig. 10--The internal-friction spectrum of the α peak in polycrystalline Ta as measured at 8700 cps and a strain amplitude of $\sim 10^{-7}$; three states were measured: as prestrained ~6%, as aged in vacuum for 1 hr at 200°C, and as re-strained

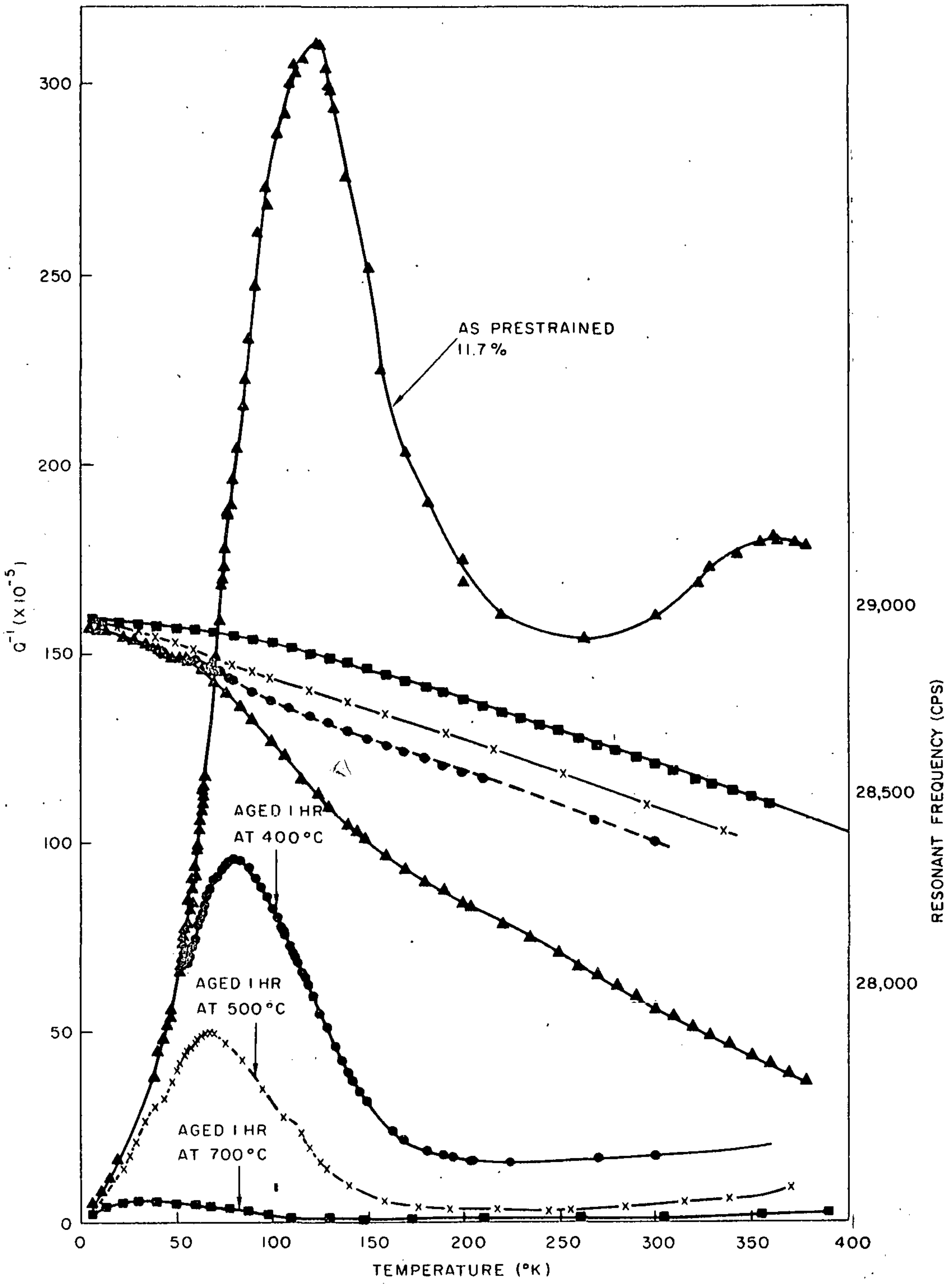

Fig. 11--Temperature variation of the internal friction and associated resonant frequency of a longitudinally oscillating specimen (Mo-3) of polycrystalline Mo; specimen was prestrained 11.7% in tension and subsequently aged in vacuum for 1 hr at various temperatures; measuring strain amplitude was ~10^{-7}

$\overline{\Delta M}/\overline{M}$, where $\overline{\Delta M}/\overline{M}$ is the fractional effective Young's modulus change. Thus the dependence of the frequency on temperature may be considered a rather accurate measure of the change with temperature of the effective Young's modulus. It can be seen from Fig. 11 that, whereas the room-temperature frequency (and thus the modulus) increases with each isochronal aging at a successively higher temperature, the 5°K frequency is barely increased by aging up to 700°C. In an independent annealing experiment, in which the specimen was aged at 800°C for 1 hr, very little change in the shape of the curve was noted from that observed after the 700°C aging treatment of specimen Mo-3, so that the 800°C curve was taken to represent the strictly elastic component of the modulus. Thus, the dislocation component of the modulus, ΔM, can be evaluated by subtracting the purely elastic-modulus component from the effective modulus, giving ΔM. The resulting modulus defect resulting from dislocation motion, $\Delta M/M$, is plotted in Fig. 12 as a function of temperature.

The quantity $\Delta M/M$ evaluated at 250°K should represent the completely relaxed α-peak modulus defect. If the α peak is a single relaxation process, the quantity $P \equiv (\Delta M/M)/Q_m^{-1}$, where Q_m^{-1} is the height of the α peak, should equal 2.(28) From Figs. 11 and 12 it can be seen that P is in fact about 13.5 for specimen Mo-3 prestrained to 11.7%. From the data on polycrystalline copper obtained by Thompson and Holmes(4) it is found that the values of P range from 4 to 5, and thus $P_{Mo}/P_{Cu} \cong 3$. Thus, it can be seen that the α peak for molybdenum is about three times broader than the Bordoni peaks for copper.

Since only isochronal measurements were made of the effect of thermal aging on the internal friction and modulus temperature dependence, only a rough estimate can be made of the activation energies that are associated with the aging process. If one assumes a strain-aging law of the form considered by Mura, Lautenschlager, and Brittain(29) for segregation of solute atoms to dislocations and, further, assumes a diffusion distance $L = 5 \times 10^{-6}$ cm based on a rough estimate of the dislocation density and an α

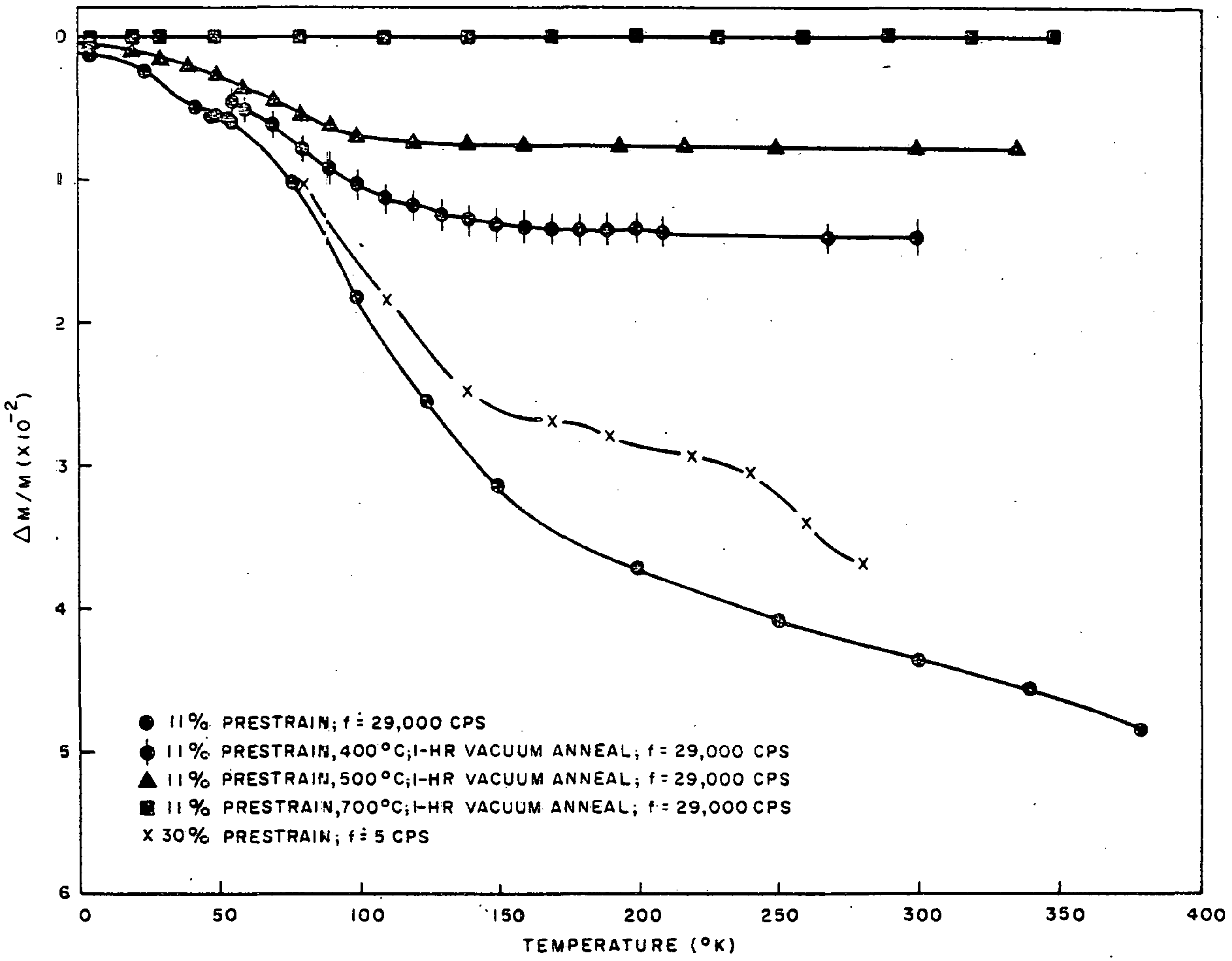

Fig. 12--Temperature dependence of the dislocation contribution to the modulus in polycrystalline Mo prestrained in tension 11.7% at room temperature and subsequently aged for 1 hr at various temperatures; specimen as aged for 1 hr at 800°C taken as the purely elastic component

value for D_0 of $\sim 10^{-2}$ cm^2/sec, then the following activation energies can be associated with the disappearance of various parts of the internal friction spectrum: 30° to 300°C (Stage I) goes with an activation energy of about 1.2 ev; 300° to 400°C (Stage II) with 1.4 ev; and 400° to 700°C (Stage III) with 2.2 ev. These energies for the various aging stages can be compared with the energy of diffusion of nitrogen, 1.15 ev;(30) carbon, 1.45 ev;(31) and oxygen, 2.09 ev.(32) The data of Martin(33) gives 1.2 ev for vacancies (or divacancies). Thus, one can assign nitrogen and vacancies to Stage I, carbon to Stage II, and oxygen to Stage III. It is believed that metallic solutes have activation energies in excess of about 2.6 ev, so that pinning by a metallic solute seems to be ruled out.

The question arises as to why the dislocations that correspond to the lower-temperature part of the α peak do not become pinned during Stages I and II. A possible explanation may be drawn from observations made by Hull and Mogford.(34) Using a transmission-electron microscope, they observed the formation of preferential carbon decoration of some types of dislocations in carbon-doped iron following strain aging. It may be that even in the bcc structures dislocations of the edge type have a higher effective interaction potential for impurities than have dislocations of the screw type. Thus, Stage III aging could correspond to the pinning of the remaining screw dislocations of the α peak population by oxygen interstitials.

Effect of Impurities on the As-deformed Internal-friction Spectrum

This section considers the influence the amount of impurities in a metal has on its deformation peak structure A measure of the total amount of impurities (the ratio Γ of the room-temperature resistance to the resistance measured at helium temperatures) was obtained on annealed samples, and individual carbon and gas analyses then gave a rough idea of the division between the amounts of interstitials and metallic impurities. A rough conversion between Γ and the total impurity concentration, c, was obtained from $c = 1/37\Gamma$. This conversion was based on the assumption that all the impurities scatter electrons as do interstitial nitrogen and oxygen in tantalum.(35)

Figure 13 shows the internal friction spectrum obtained from the relatively impure molybdenum specimens Mo-1 and Mo-3, which were prestrained to 2% and 11.7%, respectively. Shown with these specimens are the results of spectra obtained on specimen Mo-Z, which was deformed in torsion to ~1.8% and then to a total of ~8.5%. Notice the strong rise in background beyond the α peak in specimen Mo-Z. The internal-friction spectrum is similar to the results obtained by Thompson and Holmes from single-crystal copper deformed in tension to 3.25%.(4)

Figure 14 shows the internal-friction spectrum of a 40-mil specimen of as-received tantalum obtained from National Research Corporation measured at 7 cps. This specimen, Ta-8, was given a 10-min anneal at ~1500°C and then twisted at room temperature to 12% surface strain.

In the same figure is plotted the internal-friction spectrum of specimen Ta-6, measured also at 7 cps, deformed at room temperature in torsion to ~14% surface strain. Specimen Ta-6, as discussed in the section on specimen preparation, is from the same stock material as specimen Ta-8, but had a decarburizing and degassing treatment. Measurements of the low-temperature residual resistivity of this specimen indicate that the interstitial impurity content probably does not exceed ~20 at. ppm and may be even less, the remaining impurities being metallic. The internal-friction spectrum of specimen Ta-6 has a strong background component that rises after the α peak (115°K for 6 cps) and once again after the β peak (208°K). For a very large deformation of 53%, the α and β peaks merge; and the background component following the β peak is reduced considerably (this is not shown in Fig. 14). Similar deformation effects are evident at much smaller strains (~1%) in the work on polycrystalline copper by Niblett and Wilks.(36) Thermal aging of this heavily cold-worked tantalum for 1 hr at 500°C produced a considerable reduction in the over-all internal friction and <u>increased</u> the breakaway amplitude, whereas evidence of the α peak

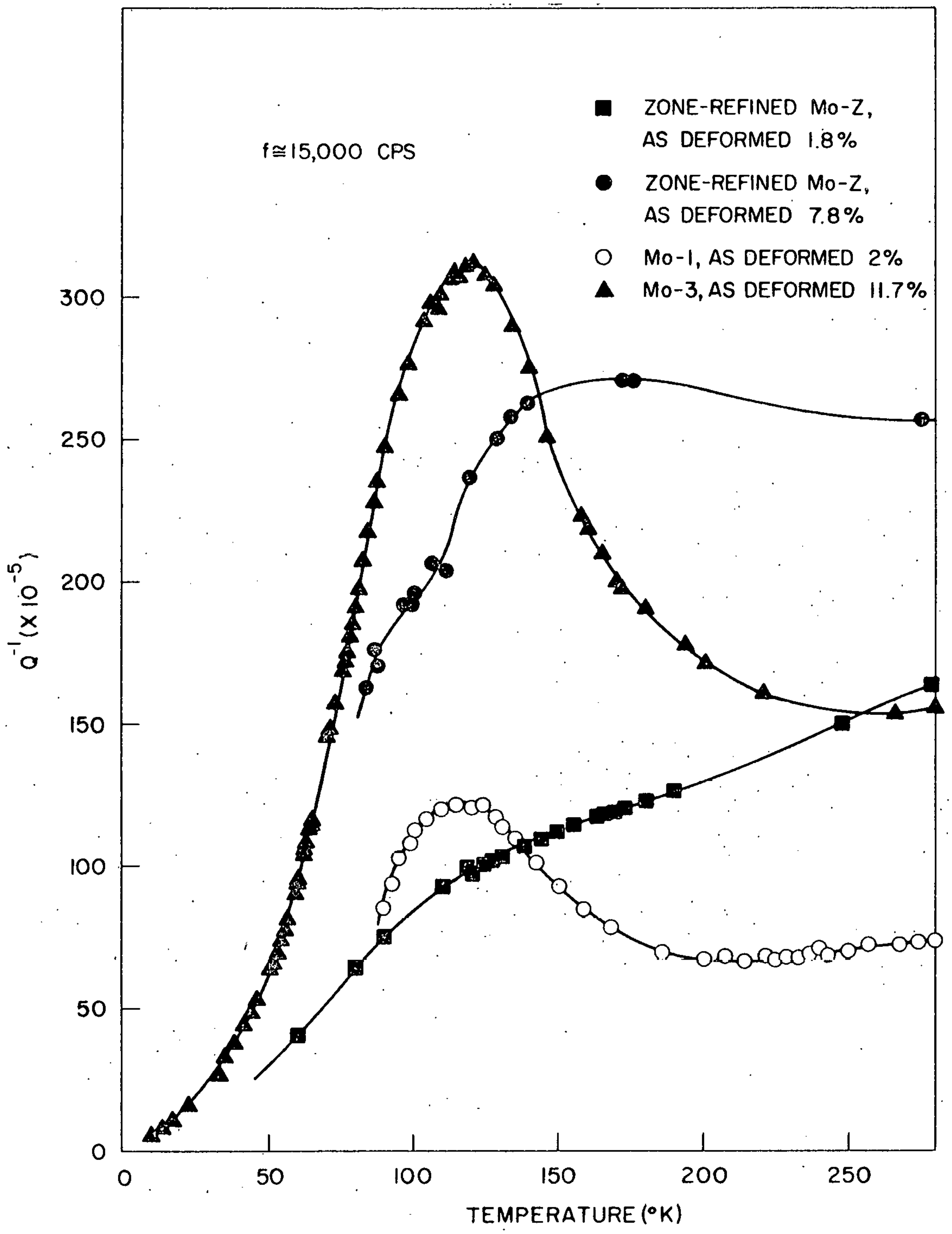

Fig. 13--The effect of purity on the internal-friction spectrum of as-plastically-deformed Mo

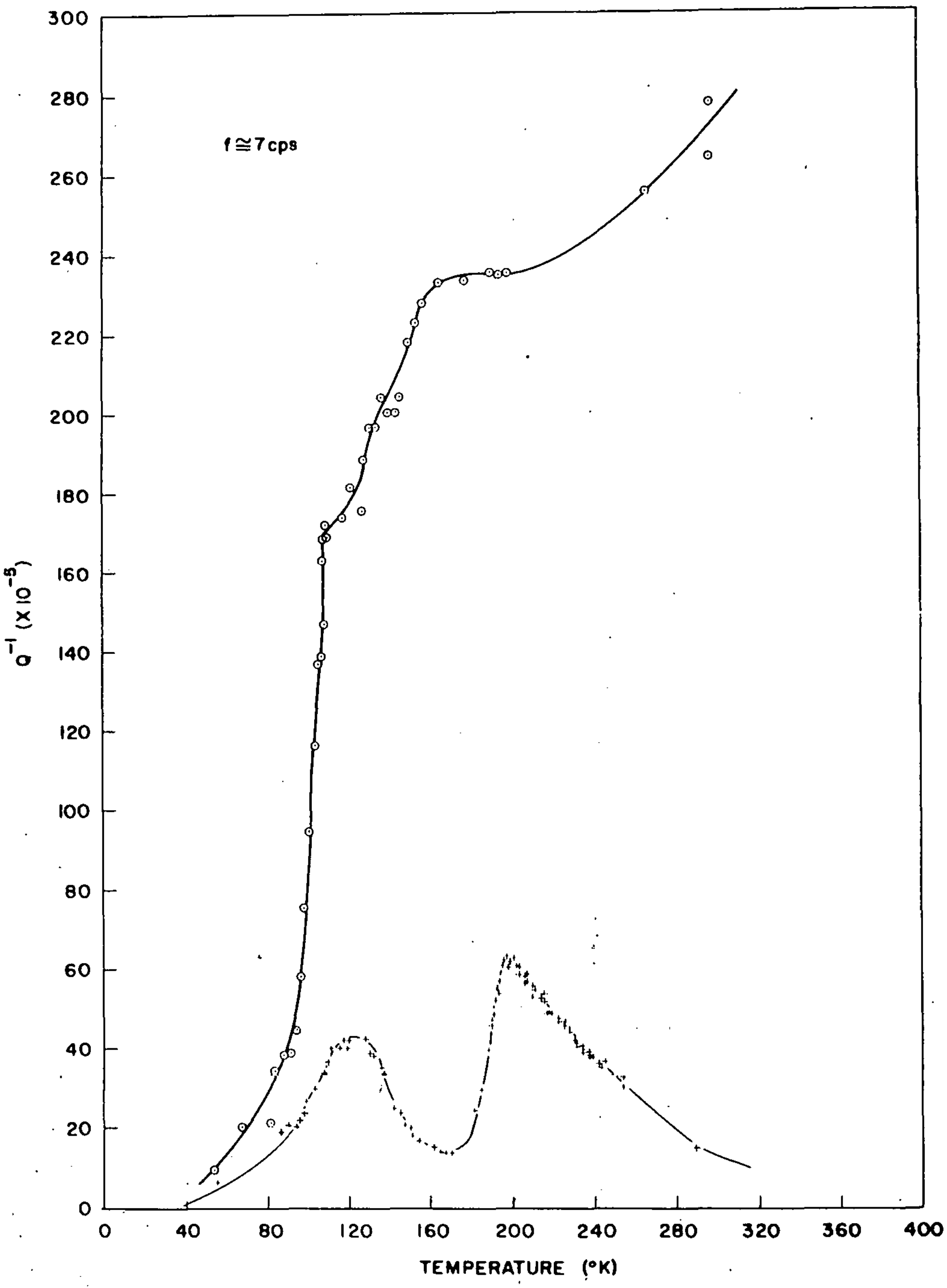

Fig. 14--The effect of interstitial impurities on the internal-friction spectrum of as-deformed Ta; the lower curve is the spectra of as-received NRC Ta annealed at 1500°C for 10 min in vacuum and twisted at room temperature to ~12% surface strain; the upper curve is same stock but with most interstitial impurities removed and twisted at room temperature to about 14% surface strain; measurements were made at ~7 cps at surface strain amplitude of ~1 × 10^{-7}

remained. It is important to note that thermal aging of less-pure tantalum, specimen Ta-8 for the same time and at the same temperature removed all trace of both the α and β peaks.

V. SUMMARY OF RESULTS

The experimental results described above can be summarized as follows: There exist two relatively broad, thermally activated relaxation peaks in the internal-friction versus temperature curves of plastically deformed niobium, tantalum, and molybdenum. Each "peak" consists of a collection of component peaks, each with a different relaxation time. The α peaks of niobium and tantalum are about the breadth of the Bordoni peak for copper, whereas the α peaks of molybdenum and tungsten are from three to four times as broad.

For a given specimen purity, the size and position of the internal-friction peaks depend primarily on the amount of prior plastic deformation. The peak heights increase monotonically for small amounts of prestrain, reach a maximum for a certain critical prestrain that depends primarily on impurity content, and finally diminish for large prestrains. The peak temperatures generally increase with prestrain, the size of the increase being larger the purer the metal. In the most extensively studied metal, molybdenum, the height of the α peak becomes larger than the β peak for prestrains greater than 5%. The α peak has been observed to shift as much as $25^{\circ}K$ with the prestrain varying from 0.1% up to several per cent. No peaks have been observed in well-annealed specimens of tantalum, niobium, molybdenum, or tungsten in the temperature and frequency range covered in this investigation.

For specimens with several hundred parts per million of interstitial impurities, the peaks are removed and large increases in the breakaway strain amplitude result from a relatively low-temperature anneal (thermal aging). The aging phenomenon can be correlated with the diffusion of interstitials over distances of the order of several hundred atom distances. As the interstitial content is lowered, an internal-friction background component appears on the high-temperature side of the relaxation peak in the as-deformed but unaged specimens. This background component is the first to be suppressed during thermal aging, followed next by the β peaks, whereas the lowest-temperature components of the α peaks are the most resistent to thermal aging. The purer the specimen, the higher must be the temperature of the isochronal anneal to produce a given reduction in the height of the peaks.

Annealing a 12% cold-worked molybdenum specimen at a temperature just under the temperature limits for recrystallization produces an increase of as much as 5% in the effective Young's modulus at 400°K but an increase no larger than 0.1% at 5°K.

VI. DISCUSSION OF RESULTS

In order to compare the various peak activation energies, attempt frequencies, and activation-energy distributions, the basis of comparison will be the most studied peak, the Bordoni peak in copper. It can be seen from Table 2 that the energies of the α peaks in niobium, tantalum, and tungsten are about twice that of the Bordoni peak in copper, whereas the energies of the β peaks in niobium, molybdenum, and tantalum are close to four times that energy. The attempt frequencies for all the bcc peaks lie in the two decades from 10^{10} to 10^{12} sec^{-1}, with most of the attempt frequencies being close to 10^{11} sec^{-1}. These values are slightly lower than the band of values (2×10^{11} to 4×10^{12} sec^{-1}) available in the literature for the Bordoni peaks in copper. As discussed by Niblett,(15) a crude measure of the distribution of activation energies contained in a given peak can be obtained from the slope of the best line through the points in a reciprocal-peak-width versus reciprocal-peak-temperature plot. From Fig. 4 it can be seen that the α peaks in tantalum and niobium have about the same breadth to their energy distribution as the copper peak. The α peaks of molybdenum and tungsten have similar distributions and have an energy distribution four times broader than is found in the Bordoni peak in copper. This estimate of the breadth of the energy distribution in the α peaks of molybdenum and tungsten compares well with that found for molybdenum specimen Mo-3 by using modulus-defect data (see "Effect of Thermal Aging" above).

Turning now to the effect of prestrain on the heights of the deformation peaks, it is interesting to compare for the bcc metals and for copper the amount of cold work necessary to produce a maximum in the relation between internal-friction peak height and the amount of prestrain. In pure copper single crystals this maximum occurs in the region between 1% and 5% prestrain; whereas in the purest bcc specimens measured, this maximum lies between 20% and 40%. Even in relatively impure specimen Mo-3, the α peak reached its maximum near 15%, and the β peak between 20% and 30%.

On the basis of these results it would appear that dislocation-dislocation pinning is more efficient in copper than in either tantalum, niobium, or molybdenum.

Another, and perhaps principal, difference in the behavior of the internal-friction spectra these two classes of metals is the response of the spectra to low-temperature annealing. The fcc metals begin to show a modification of their spectra only with the beginning of recovery, and their spectra are removed only when recrystallization commences.(37) By contrast, all of the relatively impure bcc metals studied here showed evidence of spectrum modification, such as an increase in the room-temperature modulus and an increase in breakaway amplitude, at temperatures considerably below that necessary for either recovery or recrystallization to occur. It has been shown in Section IV, "Effect of Thermal Aging," that these aging temperatures are consistent with those necessary to form a Cottrell atmosphere that is composed of impurity interstitials that act to pin those dislocations which produce the relaxation peaks.

From this picture, one would conclude that as the quantity of interstitial impurities is decreased, the annealing characteristics of the bcc peaks would tend to become more like those in fcc metals. Experiments with very pure tantalum confirm this trend. However, since the relatively strong binding energy of the impurity interstitials to dislocations in the bcc metals makes them very efficient pinning points, the total interstitial content would probably have to be lowered to ~1 part in 10^7 to begin to have the temperature insensitivity shown in the fcc metals. Therefore, the strain-aging effects noted herein probably will be evident in most studies with these metals.

One of the most interesting consequences of the aging phenomenon is the modification it produces in the Young's modulus versus temperature curves. Since it has been observed that very little change is produced in these curves between an anneal at 700°C for 1 hr and an anneal at 800°C for 1 hr and since the internal friction is reduced to less than 2×10^{-5} throughout the entire temperature range, it is believed that the 700°C, 1-hr anneal curve represents the strictly elastic component of the modulus. Hence, the dislocation component can be considered to be represented by the modulus defect $\Delta M/M$ discussed in Section IV, "Effect of Thermal Aging," and shown plotted versus temperature in Fig. 12 for specimen Mo-3. It is clear from this figure that the as-deformed molybdenum contains only a very small fraction of dislocations that are not restricted in their motion either by thermal activation or by strong pinning points. If this were not so, the modulus measured at 0°K would increase considerably more than the 0.1% it actually does increase through the pinning of those dislocations able to move at 0°K. Thus, these results for molybdenum differ significantly from those obtained by Alers and Thompson(14) in a very pure copper specimen that had been deformed 5.2%. They found that there existed a modulus defect of over 1% at 0°K in this specimen. They also found, on irradiating the sample, that about 0.25% remained at 0°K. This remaining modulus defect at 0°K was still about the same size as the entire relaxation strength of the Bordoni peaks. The 0°K background component of internal friction and modulus thus plays a dominant part in the cold-worked spectrum of pure copper, whereas its part was very negligible in specimen Mo-3.

This result implies, then, the interesting consequence that essentially all glissile dislocations in bcc molybdenum are thermally activated. Otherwise, one must assume that for some reason only those dislocations that are not thermally activated (i. e., those that would be otherwise free to move at $0^{o}K$) are pinned by impurities, whereas the thermally activated dislocations have been pulled loose from their pinning points during the plastic deformation. Since there does not seem to be any simple reason for such a preferential distribution of pinning points, the latter possibility seems unlikely.

It is now clear that the deformation-induced peaks observed here resemble in some ways the Bordoni and subsidiary peaks seen in fcc copper. This similarity between the two internal-friction phenomena becomes stronger as the impurity content of the bcc metals decreases. This can be seen by comparing the spectra of specimen Ta-6 to that of the lightly deformed copper single crystals studied by Thompson and Holmes.(4)

Thompson and Holmes suggest that the rapid rise in the background internal friction at temperatures just above those of their two principal groups of peaks is indicative of the beginning of the operation of a dislocation bowing mechanism. For small stresses and temperatures below the relaxation peaks, they consider that the dislocations are confined behind their lattice energy barriers. In this state any extensive dislocation excursions are not possible. As the temperature is raised to a point where elementary relaxation motions can occur, the relaxation peak reaches its maximum and then begins to drop as the now more mobile dislocations move more in phase with the applied stress. It is at this temperature that the elementary relaxation motions begin to combine to produce a general bowing of the dislocation line as a whole. Such a bowing motion now introduces a general viscous drag on the dislocations, which produces additional internal friction at temperatures high enough to have considerably reduced the relaxation component. As the temperature is raised still further, the bowing component should saturate, leaving a relatively temperature-independent background internal friction. At still higher temperatures any additional rise in the internal friction means either that a second relaxation process is being approached (e. g., the β peak above the α peak in the molybdenum sample shown in Fig. 13) or that there will be a thermal release from impurity pinning points (above the β peak in tantalum, shown in Fig. 14).

If enough pinning points are added to the dislocation line, the bowing component will disappear as long as the applied stress is not large enough to produce unpinning. If still more pinning points are added, even the relaxation component should be removed as long as unpinning cannot occur. In most of the relaxation peaks discussed in this paper, it is believed that enough pinning points existed, either as interstitial impurities in solid solution or as dislocation-dislocation interactions, to suppress the post-relaxation bowing motion of dislocations. In specimens that were particularly low in interstitial impurities, Mo-Z and Ta-6, the pinning concentration apparently was low enough to allow the bowing motion to occur. Specimen Ta-6 was cold-worked to several times that shown in Fig. 14 and, as a result, the internal friction above the β peaks dropped to about one-tenth the height of the β peak, thus showing, evidently, the results of dislocation-dislocation pinning.

Another observation that could be interpreted in terms of the model of dislocation motion mentioned above is seen in the internal-friction spectrum of prestrained tungsten. Figure 9 shows the α peak of specimen W-1 after two states of prestrain at about 400°C. The spectrum of this specimen was measured at various oscillating-strain amplitudes ranging from about 1×10^{-7} up to 3×10^{-5}. It is seen that the spectrum when measured at a strain amplitude of 3×10^{-5} has what looks like a post-relaxation bowing component, whereas for measuring strains of the order of 10^{-7} the bowing component is suppressed. This situation may be the result of a lightly pinned dislocation network in which unpinning can be produced relatively easily by small oscillating stresses in a manner described by Granato and Lücke;(38)(39) the extra internal friction would then be the sum of the viscous bowing component and the hysteresis component arising from the breakaway from pinning points.

VII. SUMMARY AND CONCLUSIONS

Pairs of broad, thermally activated stress-relaxation peaks were produced by room-temperature plastic deformation of the bcc transition metals niobium, tantalum, and molybdenum. At least one peak and perhaps two existed in hot-worked tungsten. The effective activation energies of these peaks were measured by internal-friction methods at frequencies from 5 to 100,000 cps and at strain amplitudes near 10^{-7}. The activation energy of the α peaks was about twice the energy of the Bordoni peak in copper; the β peaks were about four times that energy; the attempt frequencies of both peaks were comparable to if not slightly lower than those in copper.

The mechanical-relaxation phenomena observed here are interpreted in terms of some kind of thermally activated motion of segments of dislocation lines over intrinsic lattice-potential barriers.

Relatively low-temperature (approximately one-quarter of the recrystallization temperature) anneals produce a lowering of the peak heights as well as a decrease in the peak temperature. These thermal-aging effects are interpreted as being due to the pinning of the thermally activated dislocations by point defects that are produced either by the cold work or by interstitial impurities that are already present. Metallic impurities are ruled out as playing an active role in the pinning process.

Measurements on cold-worked molybdenum and tantalum containing relatively small amounts of interstitial impurities showed evidence of a postrelaxation rise in the background internal friction similar to that found in lightly cold-worked copper single crystals by Thompson and Holmes, who attributed the rise to the beginning of a bowing motion by the dislocations. Increased amounts of impurities (interstitials) and/or heavy cold working sharply reduce this background contribution in tantalum in much the same manner as observed in copper. Also, the peak temperature and peak height for a given amount of prestrain are lower for larger amounts of impurities.

A thermal-aging treatment at temperatures just under the recrystallization temperature produces a large increase in the modulus as measured at room temperature but very little change as measured at 5°K. This fact demonstrates that, contrary to the results obtained with copper, only a very small fraction of the dislocations in cold-worked bcc molybdenum are free to move at 0°K; i. e., almost all of the dislocations in molybdenum must be thermally activated over barriers that, generally, are considerably larger than those found in the fcc metals.

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