

## Temperature Dependence of the Elastic Constants of Molybdenum\*

J. M. DICKINSON AND P. E. ARMSTRONG

*University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico*

(Received 3 October 1966)

The elastic properties of molybdenum single crystals have been measured using thin-rod resonance techniques as a function of temperature from  $-198^{\circ}$  to over  $+650^{\circ}\text{C}$ . Molybdenum behaves in a normal manner over this temperature range. Its elastic stiffness coefficients, with the exception of  $C_{12}$  which increased 3%, decreased in a nearly linear manner. The decrease was 8% for  $C_{44}$ , 11% for  $C_{11}$ , and 18% for  $C'$ . From these data the temperature dependence of the bulk modulus, the shear coefficient  $C'$ , the anisotropy ratio, and the Young's and shear modulus of isotropic polycrystalline molybdenum were calculated.

### INTRODUCTION

THE elastic behavior of molybdenum is of interest because of the importance of this metal in modern technology. Molybdenum is also one of the few pure cubic metals whose resistance to elastic shear deformation across (100) planes is less than that across (110) planes, resulting in values less than unity for the anisotropy factor as defined by Zener.<sup>1</sup> The same relative change in magnitude of the shear elastic constants with temperature for crystals with anisotropy factors less than or greater than unity produces distinctly different changes in elastic stiffness coefficients for dilatational deformation modes. In the case of niobium metal, for example, the authors<sup>2</sup> have shown that Young's modulus measured in directions other than [100] actually increased with temperature, over at least a  $1100^{\circ}\text{C}$  temperature range. The purposes of this investigation were, then, twofold: first, to extend the temperature range of previously reported measurements, and second, to detect the presence of any anomalies at elevated temperatures that might be comparable to the behavior of niobium.

### EXPERIMENTAL PROCEDURE AND SPECIMEN PREPARATION

Single crystals of electron-beam-melted molybdenum metal were obtained from Semi-Elements Inc. in the form of rods, approximately 0.6-cm-diam by 13-cm-long. These crystals were ground to a uniform diameter ( $\pm 0.001\text{-cm}$ ) and cut to 10-cm lengths. The ends were ground flat and parallel using metallographical procedures. After a light chemical etch ( $\text{HNO}_3 + \text{HF}$ ) the crystals were annealed 2 h at  $2100^{\circ}\text{C}$  in a vacuum of  $1 \times 10^{-6}$  Torr and furnace cooled.

The orientation function,  $\Phi = \alpha^2\beta^2 + \alpha^2\gamma^2 + \beta^2\gamma^2$  where  $\alpha$ ,  $\beta$ , and  $\gamma$  are the direction cosines of the sample rod axis, was determined for each molybdenum crystal using standard x-ray diffraction methods. The crystals had either the [100], [110], or [111] nearly parallel

to their cylinder axis. The orientation functions of these crystals are shown in Table I.

A single crystal of molybdenum 1.6 cm diameter by 12 cm long was obtained from the Linde Company. The rod axis was between the [100] and [110]. Two specimens approximately 1-cm-thick were prepared from this rod, one having parallel faces cut perpendicular to a [100] and the other having parallel faces cut perpendicular to a [110].

Chemical analyses were performed on the specimens using standard spectrographical techniques except that

TABLE I. Crystallographic orientation of molybdenum specimens.

Crystal	Cylinder axis direction	$\Phi$
Semi-Elements <i>a</i>	[100]	0.0047
Semi-Elements <i>b</i>	[100]	0.0015
Semi-Elements <i>c</i>	[110]	0.251
Semi-Elements <i>x</i>	[111]	0.331

oxygen was determined by vacuum fusion, nitrogen by a modified Kjeldahl method, and carbon by combustion. The results are given in Table II. Elements not shown in Table II were below normal limits of detection.

### MEASUREMENTS OF ELASTIC PROPERTIES

The data necessary to determine the elastic properties of molybdenum were obtained from the thin-rod free-free resonance measurements using instrumentation described previously by the authors.<sup>3</sup> A separate instrumentation package also employing capacitive probes for the excitation and detection of longitudinal resonances and eddy-current probes for the excitation and detection of torsional resonances was constructed to fit in a cryostat for measurements below room temperature.

High-frequency pulse-transmission techniques were used with the Linde crystals at room temperature. Measurements were made at 10 Mc/sec employing an Arenberg model 650 PG pulsed oscillator, a Tek-

<sup>3</sup> P. E. Armstrong and J. M. Dickinson, *Rev. Sci. Inst.* **36**, 1719 (1965).

\* Work performed under the auspices of the U.S. Atomic Commission.

<sup>1</sup> C. Zener, *Elastic and Anelasticity of Metals* (Univ. of Chicago Press, Chicago, Ill., 1948).

<sup>2</sup> P. E. Armstrong and H. L. Brown, *Trans. ASM* **58**, 30 (1965).

tronics model 547 oscilloscope, and X and Y cut quartz driver and detector crystals.

Low temperatures were measured using a calibrated copper-constantan thermocouple, while high temperatures were measured using a chromel-alumel thermocouple. The temperature ranges of the two apparatus overlapped so that an internal check on the instruments and specimens was provided.

DATA TREATMENT

The experimental data were treated in much the same way as the work on niobium reported earlier by the authors.<sup>4</sup> Briefly, plots were made of the fundamental resonance frequency vs temperature for both the longitudinal and torsional vibration modes for each of the four crystals over the temperature range from -200°C to approximately 660°C. Resonance frequencies were then determined graphically for both vibrational modes of each crystal at 20°C intervals. This method circumvented the necessity of taking the measurements on each crystal at exactly the same temperature.

Corrections for changes in the length and density of the specimen were made using a mean linear thermal expansion coefficient of  $5.31 \times 10^{-6}$  per °C. Knowing the temperature, resonance frequency, specimen length and density, and the thermal expansion coefficient, the moduli were calculated from the following equation:

$$\text{Modulus } (E \text{ or } G) = 4l^2 f^2 \rho (1 + \alpha \Delta T)^{-1},$$

where  $f$  is the resonance frequency, longitudinal if  $E$  is being calculated and torsional if  $G$  is being calculated,  $l$  is the specimen length,  $\rho$  is the specimen density,  $\alpha$  is the thermal expansion coefficient, and  $\Delta T$  is the difference between 25°C and the temperature. Using cgs units the modulus is given in  $\text{dyn}\cdot\text{cm}^{-2}$ .

The calculated values of Young's and shear moduli were combined with the measured orientation functions to calculate the elastic stiffness coefficients. The calculations were made on a computer using a least

TABLE II. Chemical analysis of Mo specimens.

	Semi-Element crystals (ppm)	Linde crystals (ppm)
O <sub>2</sub>	40 to 80	10 to 30
N <sub>2</sub>	40	30
C	30	30
Ni	30	<10
Cu	5	<3

<sup>4</sup> P. E. Armstrong, J. M. Dickinson, and H. L. Brown, Trans. AIME 236, 1404 (1966).

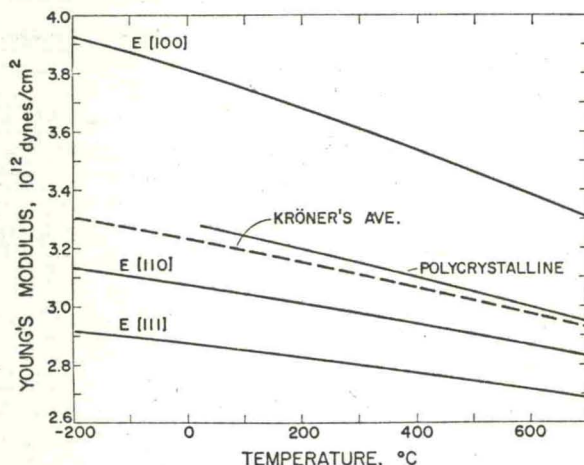


FIG. 1. The variations with temperature of Young's modulus of three single crystals of molybdenum, Young's modulus of fine-grained polycrystalline molybdenum, and Young's modulus calculated for isotropic molybdenum from the single-crystal data.

squares fitting program with Eqs. (1) and (2):

$$E^{-1} = -\{[2/(C_{11} - C_{12})] - C_{44}^{-1}\} \Phi + \frac{1}{3}\{[2/(C_{11} - C_{12})] + (C_{11} + 2C_{12})^{-1}\} \quad (1)$$

$$G^{-1} = 2\{[2/(C_{11} - C_{12})] - C_{44}^{-1}\} \Phi + [C_{44}^{-1}]. \quad (2)$$

Since data from four crystals were used, eight equations in three unknowns could be fitted at each temperature and a reasonable estimate of the standard deviation of each of the elastic constants could be obtained.

From the calculated  $C_{ij}$ 's other parameters were determined using Zener's notation as:

$C \equiv C_{44}$ —the coefficient indicating resistance to shear between (100) planes in the [010] direction.

$C' = (C_{11} - C_{12})/2$ —the coefficient indicating resistance to shear between (110) planes in the [110] direction.

$K = (C_{11} + 2C_{12})/3$ —the bulk modulus.

$A = C/C'$ —the anisotropy ratio.

RESULTS

The results of this investigation have been presented as a series of graphs. These graphs, Figs. 1 to 8, have been plotted to the same scale so that the slopes are directly comparable by observation.

As is normal for most metals in this temperature range, Young's modulus and shear modulus decreased almost linearly with increasing temperature, as shown in Figs. 1 and 2. The change in Young's modulus with temperature was largest for the [100] direction, dropping nearly 16% over the 860°C temperature range while the change was about 8% for the [111] direction. The shear modulus for the [111] direction decreased 14% while the decrease was 8% in the

functions of

diameter by  
de Company.  
[110]. Two  
were prepared  
cut perpen-  
parallel faces

the specimens  
es except that

enum specimens.

Φ

0.0047

0.0015

0.251

0.331

usion, nitrogen  
carbon by com-  
e II. Elements  
ormal limits of

PROPERTIES

lastic properties  
e thin-rod free-  
instrumentation  
A separate in-  
capacitive probes  
ngitudinal reso-  
excitation and  
constructed to  
low room tem-

techniques were  
m temperature.  
sec employing  
scillator, a Tek-  
Rev. Sci. Inst. 36.

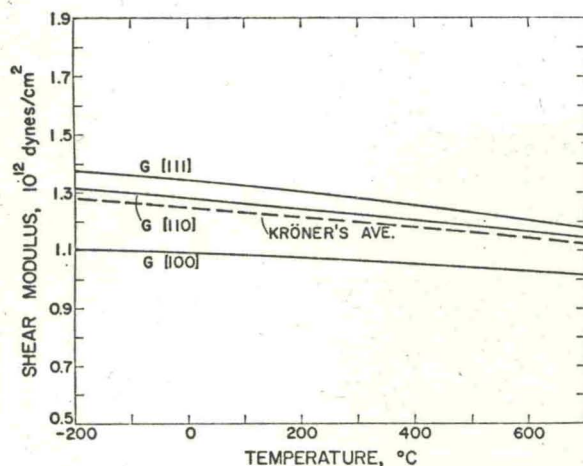


FIG. 2. The variations with temperature of the shear modulus of three single crystals of molybdenum, and the shear modulus calculated for isotropic molybdenum from the single-crystal values.

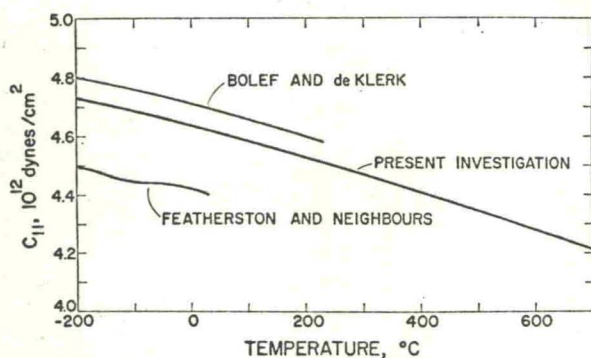


FIG. 3. The elastic stiffness coefficient  $C_{11}$  of molybdenum as a function of temperature.

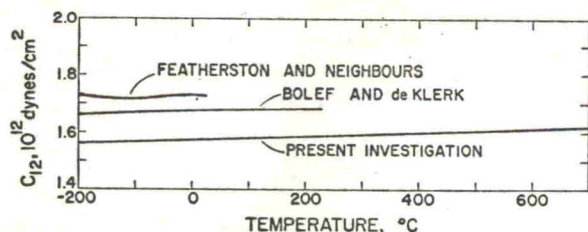


FIG. 4. The elastic stiffness coefficient  $C_{12}$  of molybdenum as a function of temperature.

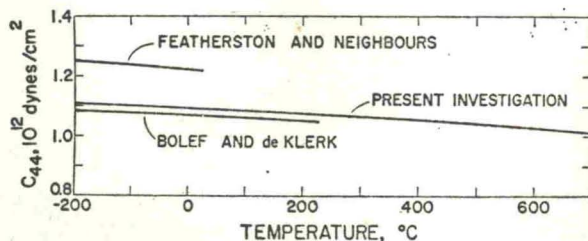


FIG. 5. The elastic stiffness coefficient  $C_{44}$  of molybdenum as a function of temperature.

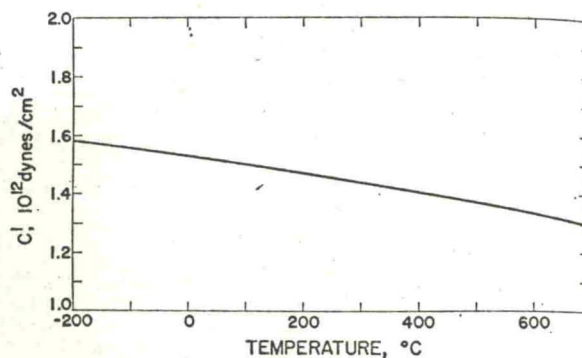


FIG. 6. The shear coefficient  $C'$  as a function of temperature.

[100] direction. At each temperature, the [100] direction showed the largest Young's modulus and smallest shear modulus while the [111] direction had the largest shear modulus and smallest Young's modulus, resulting in an anisotropy factor less than unity.

The elastic stiffness coefficients calculated from the experimental data are shown plotted against temperature in Figs. 3, 4, and 5. Coefficients  $C_{11}$  and  $C_{44}$  again showed a decrease with increasing temperature, the decrease amounting to about 11% for  $C_{11}$  and 8% for  $C_{44}$ .  $C_{12}$ , on the other hand, actually showed a small increase. In Table III the values of the elastic stiffness coefficients of Mo and the estimated standard deviations are shown at 100°C intervals.

Since the elastic stiffness coefficient  $C_{12}$  has no simple physical interpretation, it is desirable to also report the data in terms of combinations of coefficients that have a physical significance. The bulk modulus,  $K$ , and the shear coefficient,  $C'$ , which were defined earlier are such coefficients. Curves showing the variation of these two coefficients with temperature are shown in Figs. 6 and 7. The bulk modulus, which measures the resistance of the material to hydrostatic compression decreases about 5% over the 900°C temperature range. The shear coefficient  $C'$  decreased 18% over the same temperature range while  $C_{44}$ , the other shear coefficient, decreased only 8%, so that their ratio, the anisotropy factor (Fig. 8), is increasing towards unity as temperature increases. This indicates a tendency

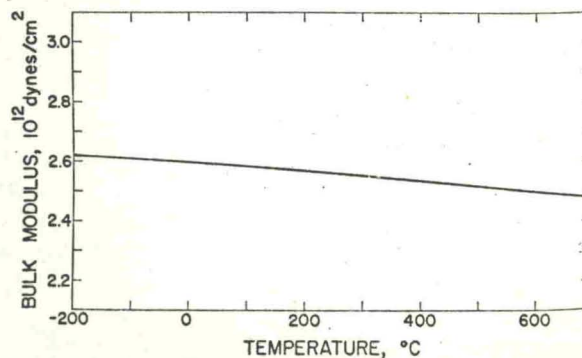


FIG. 7. The bulk modulus of molybdenum as a function of temperature.

TABLE III. Elastic stiffness coefficients of molybdenum.

Temp (°C)	$C_{11}$ $10^{12}$ dyn·cm <sup>-2</sup>	$C_{12}$ $10^{12}$ dyn·cm <sup>-2</sup>	$C_{44}$ $10^{12}$ dyn·cm <sup>-2</sup>
-200	4.730±0.094	1.562±0.099	1.109±0.0024
-100	4.688±0.083	1.569±0.088	1.101±0.0021
0	4.637±0.085	1.578±0.090	1.092±0.0021
+100	4.578±0.089	1.581±0.095	1.082±0.0022
200	4.522±0.092	1.587±0.096	1.072±0.0023
300	4.462±0.092	1.592±0.096	1.062±0.0023
400	4.403±0.094	1.598±0.099	1.051±0.0023
500	4.345±0.091	1.609±0.096	1.040±0.0022
600	4.280±0.086	1.610±0.090	1.029±0.0021
700	4.215±0.082	1.613±0.086	1.018±0.0020

towards an isotropic behavior as temperature increases.

### DISCUSSION

Several investigators have reported room temperature values for the single-crystal elastic constants of molybdenum, and two of them have also made measurements over a limited temperature range.

The room-temperature values of the elastic coefficients of molybdenum determined during previous investigations along with those determined during this study are shown in Table IV. The agreements between the pulse-transmission and thin-rod resonance values determined during the present investigation and the values reported by Bolef and de Klerk<sup>5</sup> are very good. The results reported by Druyvesteyn<sup>6</sup> are surprisingly close to these values considering that he worked with rolled sheet having a "clear texture," since single crystals of molybdenum were not available at that time (1941). The values of the elastic constants reported by Featherston and Neighbors<sup>7</sup> are in considerable disagreement with those of all the other

TABLE IV. Room-temperature elastic properties of Mo.

Investigation	Units of $10^{12}$ dyn·cm <sup>-2</sup>					
	$C_{11}$	$C_{12}$	$C_{44}$	$C'$	$K$	$A$
Featherston and Neighbors	4.4078	1.724	1.216	1.342	2.619	0.91
Bolef and de Klerk	4.696	1.675	1.068	1.510	2.683	0.71
Druyvesteyn	4.6	1.79	1.09	1.4	2.73	0.78
Present, thin rod	4.63	1.61	1.09	1.51	2.62	0.72
Present, pulse echo	4.62	1.58	1.09	1.52	2.59	0.72

<sup>5</sup> D. T. Bolef and J. de Klerk, J. Appl. Phys. **33**, 2311 (1962).

<sup>6</sup> J. Druyvesteyn, Physica **8**, 439 (1941).

<sup>7</sup> F. H. Featherston and J. R. Neighbors, Phys. Rev. **130**, 1324 (1963).

<sup>8</sup> E. Kröner, Z. Phys. **51**, 504 (1958).

<sup>9</sup> W. Voigt, Lehrbuch der Kristallphysik 962 (1928).

<sup>10</sup> A. Reuss, Z. Angew. Math. Mech. **9**, 49 (1929).

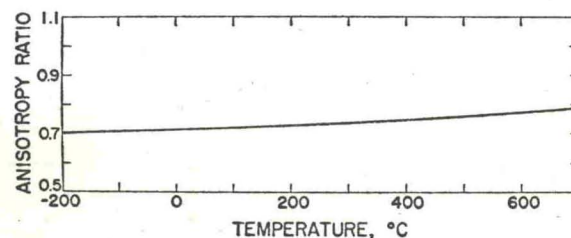


FIG. 8. The anisotropy ratio of molybdenum as a function of temperature.

investigators. The reasons for the disagreement are not completely apparent, although as they pointed out, the molybdenum used in that investigation was of low purity, e.g., containing 920 ppm oxygen.

The  $C_{ij}$ 's calculated from the data of Bolef and de Klerk, and those of Featherston and Neighbors were plotted along with those from this investigation as functions of temperature in Figs. 3, 4, and 5. Although Bolef and de Klerk did not mention it, the  $C_{12}$  curve calculated from their data shows an increase in value as temperature increases in agreement with the present results. A linear extrapolation of the  $C_{ij}$  curves to absolute zero was made. Since the elastic stiffness coefficients approach absolute zero with zero slope the values of the  $C_{ij}$ 's at zero should lie between the extrapolated values and the measured values at  $-198^\circ\text{C}$ . Table V contains these data at the two temperatures and their averages. Since the difference between the values at these temperatures is small for molybdenum their averages should be good approximations of the true values at absolute zero.

The usefulness of averaging techniques to determine the elastic moduli,  $E$  and  $G$ , for a polycrystalline material from the single-crystal elastic constants is being recognized by many investigators as a useful technique. The moduli that the material would have if it were isotropic has considerable value from a practical standpoint. Using Kröner's<sup>8</sup> method of averaging the Voigt<sup>9</sup> and Reuss<sup>10</sup> averages such calculations were

TABLE V. Elastic stiffness coefficients of molybdenum at absolute zero.

Investigation	$C_{11}$	$C_{12}$	$C_{44}$
	All in units of $10^{12}$ dyn·cm <sup>2</sup>		
Present, at $-198^{\circ}\text{C}$	$4.730 \pm 0.094$	$1.562 \pm 0.099$	$1.109 \pm 0.0024$
Present, linearly extrapolated to $-273^{\circ}\text{C}$	4.768	1.554	1.111
Average of above = value at absolute zero	4.749	1.558	1.10
Featherston and Neighbours	4.500	1.729	1.250

made for molybdenum. The calculated curve for Young's modulus is shown in Fig. 1 along with the curves of Young's modulus for the single crystals.

Earlier work by the authors<sup>11</sup> included a measurement of the Young's modulus of polycrystalline molybdenum up to  $2400^{\circ}\text{C}$  and a portion of that curve is also shown in Fig. 1. The difference between the experimental and calculated curve is within 2.3% at room temperature and less at higher temperatures.

The shear modulus for this specimen of molybdenum  $1.206 \times 10^{12}$  dyn·cm<sup>-2</sup> obtained which is in good agreement with the value of  $1.245 \times 10^{12}$  dyn·cm<sup>-2</sup> calculated from the single-crystal data.

Poisson's ratio was calculated from Young's and shear moduli for polycrystalline molybdenum using Kröner's averaging method and ranged from 0.280 at  $-200^{\circ}\text{C}$  to 0.300 at  $+700^{\circ}$ , the room temperature value being 0.293.

#### CONCLUSIONS

(1) The elastic stiffness coefficients  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ , Young's modulus  $E$ , the shear modulus  $G$ , the

<sup>11</sup> P. E. Armstrong and H. L. Brown, Trans. AIME 230, 962 (1964).

derived elastic coefficients,  $C'$ ,  $K$  and  $A$ , have been determined for molybdenum using a thin-rod resonance technique. Measurements were made on single crystals from  $-198^{\circ}$  to about  $600^{\circ}\text{C}$  and the elastic coefficients were reported from  $-273$  to  $+700^{\circ}\text{C}$ .

(2) The elastic properties of molybdenum were normal, decreasing in a nearly linear manner as temperature increased, except for  $C_{12}$  and the anisotropy ratio.

(3)  $C_{12}$  showed a small but uniform increase as temperature increased.

(4) The anisotropy ratio,  $A$ , increased toward unity as the temperature increased, the large decrease in  $C'$  with increasing temperature being the controlling factor.

(5) From the experimental data the average moduli were calculated for polycrystalline molybdenum and these also behaved in a manner typical for cubic metals.

#### ACKNOWLEDGMENTS

The authors wish to thank John O'Rourke for performing the x-ray orientation work required for this study and David Franklin for his assistance in obtaining some of the high-temperature data.