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## Elastic Constants of Tantalum, Tungsten, and Molybdenum\*

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The three elastic constants of tantalum, tungsten, and molybdenum have been measured in the temperature range between 4.2 and 300°K. The directly measured quantities  $C_L$  and  $\frac{1}{2}(C_{11}-C_{12})$  for molybdenum and the computed bulk moduli of all three elements show an anomalous temperature dependence. These data along with published results for other metals generally show a difference in temperature dependence of the bulk modulus between  $3d$  and  $4d-5d$  metals. Overlap contributions to the elastic constants are found to favor an antiferromagnetic ordering. The Debye characteristic temperatures calculated from elastic constants are found to be in substantial agreement with results obtained from calorimetry.

### INTRODUCTION

AS well as being of intrinsic interest as a physical property, the elastic constants give information concerning the nature of the forces operative in solids. Also, the low-temperature elastic constants may be used to predict the lattice heat which may be compared with the results of calorimetric measurements.

With the inception of the pulse method much work has been carried out on elastic constants of solids. Principally because of metallurgical difficulties, very few measurements have been carried out on the transition elements. However, recent advances have made available large single crystals of some of these metals.

### EXPERIMENTAL PROCEDURE

The adiabatic elastic constants of tantalum, tungsten, and molybdenum have been obtained from room temperature down to liquid-helium temperatures by measuring the transit times of elastic waves in single crystals. Unrectified waveforms were observed using an ultrasonic apparatus similar to that described previously.<sup>1,2</sup> A preliminary report on the elastic constants of tantalum pointing out anomalies in the observed bulk modulus has already been given.<sup>3</sup>

The tantalum specimen was purchased from Materials Research Corporation as a  $\frac{1}{4}$ -in.-diam rod from which a 2.0643-cm (at 20°C) specimen was cut with accurately parallel faces. Because of its small diameter, no attempt was made to orient this crystal. Instead the orientation was taken "as is". This orientation was determined by Laue back-reflection x-ray methods to deviate from  $[110]$  by about 8°, the associated polar angles being  $\theta=84.9^\circ$  and  $\phi=39.7^\circ$ . Transit time measurements were made on the tantalum specimen both before and after annealing at 1200°C for 5 h in a vacuum of at least  $10^{-5}$  mm Hg. Annealing did not

affect the observed transit times. No change in velocity or attenuation of the elastic waves was observed in passing through the superconducting transition temperature for tantalum. The transducer binder used with the tantalum sample was glycerin below 0°C and salol at and above 0°C.

Temperatures on all samples were controlled to within 0.5°C during transit time measurements using a Brown Electronik recorder. A copper-constantan thermocouple was used for all temperature measurements above liquid-air temperatures. For temperatures from liquid-air to liquid-helium temperatures a copper resistance thermometer was used when making the measurements on tantalum; a copper-gold 2.1 at. % cobalt alloy thermocouple was used for the tungsten and molybdenum measurements in the same low-temperature range.

The tungsten single crystal was purchased from the Linde Company as a  $\frac{1}{2}$ -in.-diam rod that had been grown with its longitudinal axis 2° off  $[110]$ . From this, a specimen was prepared that had two parallel faces accurately perpendicular to  $[110]$  and 2.4866 cm apart (at 0°C). Nonaq stopcock grease was used as the binder for tungsten at all temperatures.

The molybdenum single crystal was obtained from the Wah Chang Corporation as a rough surfaced bar averaging about 1 in. in diameter. Using standard Laue back-reflection techniques, a  $[110]$  direction was located in this specimen. Two parallel faces were then cut perpendicular to this direction, the mean distance between faces being 1.8322 cm at 0°C. The maximum deviation from parallelism of these surfaces in the molybdenum sample, as was also true for the tantalum and tungsten specimens, was 0.0002 cm. The transducer binder used for molybdenum was Nonaq stopcock grease for the readings at a just below room temperature and Dow Corning high vacuum grease from below these temperatures down to helium temperatures.

In calculating the elastic constants of these metals the thermal expansion data of Nix and MacNair<sup>4</sup> were used down to the limits of their validity (the liquid-air temperature region). Extrapolations from these data

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† Based upon the dissertation submitted by F. H. Featherston in partial fulfillment of the requirements for the Ph.D. degree at the U. S. Naval Postgraduate School.

<sup>1</sup> J. R. Neighbours and G. A. Alers, *Phys. Rev.* **111**, 707 (1958).

<sup>2</sup> G. A. Alers and J. R. Neighbours, *J. Phys. Chem. Solids* **7**, 58 (1958).

<sup>3</sup> F. H. Featherston and J. R. Neighbours, *Bull. Am. Phys. Soc.* **7**, 236 (1962).

<sup>4</sup> F. C. Nix and D. MacNair, *Phys. Rev.* **61**, 74 (1942).

following Grueneisen plots were used down to 4.2°K. The lattice constant used for tantalum was 3.3058 Å at 25°C, as given in a survey by Swanson and Tatge.<sup>5</sup> From this a density of 16.6324 g/cc at 0°C was calculated. For tungsten, the lattice constant given in Pearson<sup>6</sup> of 3.1650 Å at 25°C was used. The 0°C density of tungsten, using this value of lattice parameter, is 19.2710 g/cc. Pearson was also the source for the lattice constant of molybdenum, 3.1468 Å at 20°C. The 0°K density of molybdenum calculated from this value is 10.2549 g/cc.

Results of impurity analyses conducted on these three metals are contained in Table I. The analyses of tantalum and molybdenum were conducted by the firm of Kennard and Drake of Los Angeles, using test material that had been taken from the original specimens. The tungsten analysis, provided by the Linde Company, is an average analysis for material produced at the same time as the sample used. Table I shows a low metal impurity content for all three samples. The

TABLE I. Chemical and vacuum fusion analyses of crystal specimens (ppm by weight).<sup>a</sup>

Tantalum		Tungsten		Molybdenum	
Fe	20	C	10	Fe	50
Cu	3	S	10	Si	77
O <sub>2</sub>	222	Al	<100	O <sub>2</sub>	930
N <sub>2</sub>	124	Be	<100	N <sub>2</sub>	140
H <sub>2</sub>	9	Cd	<100	H <sub>2</sub>	10
		Mg	<1		
		Si	<100		
		O <sub>2</sub>	25		
		N <sub>2</sub>	<20		
		H <sub>2</sub>	1		

<sup>a</sup> All other impurities *nil*.

interstitial gas content is low for tungsten, larger for tantalum, and quite substantial for molybdenum.

### EXPERIMENTAL RESULTS

For the tantalum specimen the measured transit times were used to calculate the quantity  $\rho V^2$  for each of the three modes being propagated in a direction some 8° off [110]. Smooth lines were drawn through these raw data of  $\rho V^2$  vs temperature, yielding the curves of Fig. 1. Values were taken from these curves at regular increments of temperature and a successive approximation method due to Neighbours<sup>7</sup> was applied to derive the values of the elastic constants listed in Table II.

Since the direction of elastic wave propagation in the tungsten and molybdenum samples was directly along

<sup>5</sup> H. E. Swanson and E. Tatge, National Bureau of Standards Circular 539 (U. S. Government Printing Office, Washington 25, D. C., 1953), Vol. 1.

<sup>6</sup> W. B. Pearson, *A Handbook of Lattice Spacings & Structures of Metals and Alloys* (Pergamon Press, Ltd., London, 1958).

<sup>7</sup> J. R. Neighbours, *J. Acoust. Soc. Am.* **26**, 865 (1954).

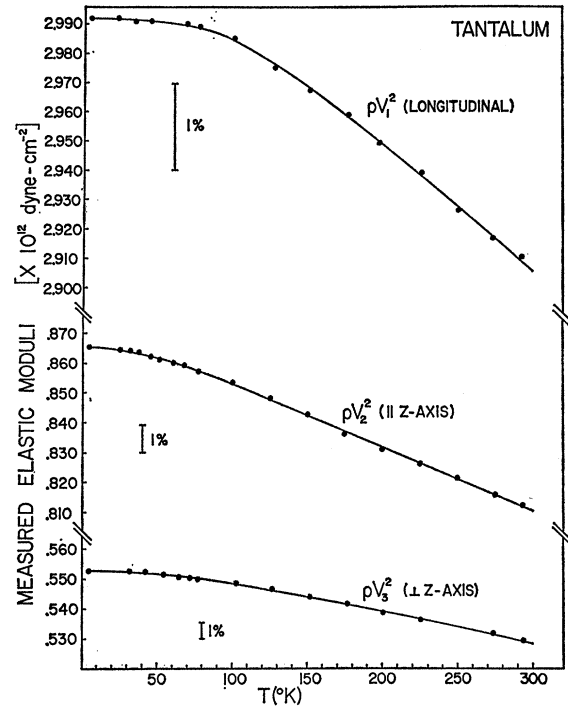


FIG. 1. Measured values of  $\rho V^2$  for tantalum as a function of temperature. The direction of elastic wave propagation for this sample was 8° removed from [110] (see text).

[110], the values of  $\rho V^2$  calculated from the transit time measurements are equal to certain linear combinations of the three adiabatic elastic constants. Accordingly, Fig. 2 displays the measured variation with temperature for the longitudinal mode  $\rho V^2 = \frac{1}{2}(C_{11} + C_{12}) + C_{44}$  in tungsten. Figure 3 displays the measured variation with temperature of the  $\rho V^2$ 's associated with the two transverse modes for tungsten. These equal  $\frac{1}{2}(C_{11} - C_{12})$  for the mode polarized perpendicular to the z axis and  $C_{44}$  for the mode polarized parallel to the z axis. Smooth curves have been drawn through the observed data points of Figs. 2 and 3, and a com-

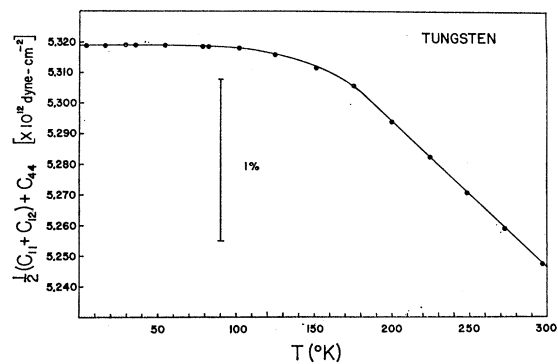


FIG. 2. The elastic constant  $\frac{1}{2}(C_{11} + C_{12}) + C_{44}$  for tungsten as a function of temperature.

TABLE II. The elastic constants of tantalum, in units of  $10^{12}$  dyn-cm $^{-2}$ , as a function of absolute temperature. Calculated by a perturbation method from smooth curves drawn through values obtained from measurements made in a direction of propagation  $8^\circ$  from  $[110]$ . The number of significant figures shows the internal consistency of the data and does not indicate the accuracy of the absolute value.

$T$ (°K)	$C_{11}$	$C_{12}$	$C_{44}$	$\frac{1}{2}(C_{11}-C_{12})$	$\frac{B}{3}$ $(C_{11}+2C_{12})$	$C_{12}-C_{44}$
0	2.6632	1.5816	0.8736	0.5408	1.9421	0.7080
20	2.6633	1.5823	0.8728	0.5405	1.9426	0.7095
40	2.6641	1.5844	0.8709	0.5398	1.9443	0.7135
60	2.6649	1.5870	0.8682	0.5390	1.9463	0.7188
80	2.6652	1.5896	0.8647	0.5378	1.9481	0.7249
100	2.6638	1.5912	0.8609	0.5363	1.9487	0.7303
120	2.6603	1.5909	0.8564	0.5347	1.9474	0.7345
140	2.6562	1.5900	0.8522	0.5331	1.9454	0.7378
160	2.6518	1.5888	0.8480	0.5315	1.9431	0.7408
180	2.6467	1.5875	0.8436	0.5296	1.9406	0.7439
200	2.6412	1.5860	0.8393	0.5276	1.9377	0.7467
220	2.6350	1.5840	0.8352	0.5255	1.9343	0.7488
240	2.6286	1.5818	0.8309	0.5234	1.9307	0.7509
260	2.6221	1.5794	0.8266	0.5214	1.9270	0.7528
280	2.6155	1.5768	0.8224	0.5194	1.9230	0.7544
300	2.6091	1.5743	0.8182	0.5174	1.9192	0.7561

pilation is presented in Table III of the adiabatic elastic constants of tungsten for values taken at regular intervals of temperature from these smooth curves.

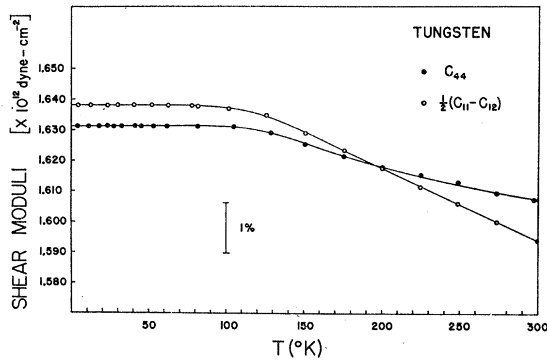


FIG. 3. The shear constants,  $C_{44}$  and  $\frac{1}{2}(C_{11}-C_{12})$ , for tungsten as functions of temperature.

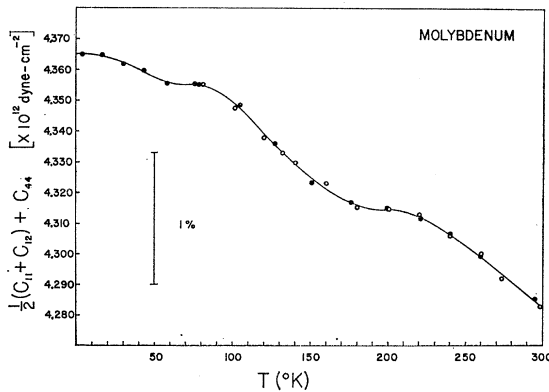


FIG. 4. The elastic constant  $\frac{1}{2}(C_{11}+C_{12})+C_{44}$  for molybdenum as a function of temperature. Two separate measurements of the constant, as indicated by open and closed circles, were made between liquid-air and room temperatures.

Correspondingly, Figs. 4 and 5 display the measured longitudinal and transverse  $\rho V^2$  for molybdenum. Table IV shows the adiabatic elastic constants of molybdenum derived from the curves depicted in Figs. 4 and 5.

Taking into account the various sources of error, we estimate the absolute accuracy of a single observation of  $\rho V^2$  to be  $\pm 0.5\%$ , although the internal consistency of the data is much better than this. Since the elastic wave propagation in the tungsten and molybdenum samples was directly along a principal direction, the above estimate of  $\pm 0.5\%$  should be valid as an estimate of error for the final reported values of the elastic constants. In the case of tantalum, however, the direction of propagation was some  $8^\circ$  off  $[110]$ . Errors attendant to determining the direction cosines of this direction necessitate degrading the estimate of absolute error of the tantalum results to  $\pm 1.0\%$ .

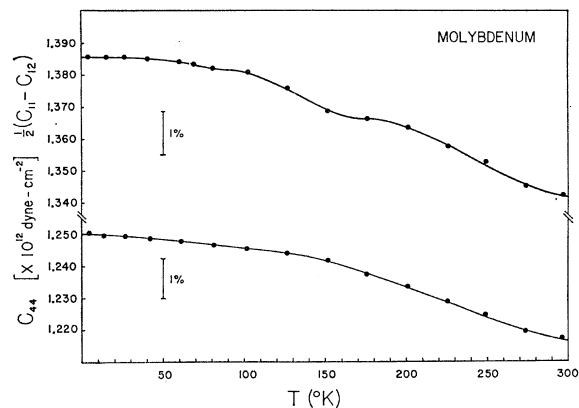


FIG. 5. The shear constants,  $C_{44}$  and  $\frac{1}{2}(C_{11}-C_{12})$ , for molybdenum as functions of temperature.

TABLE III. The elastic constants of tungsten, in units of  $10^{12}$  dyn-cm $^{-2}$ , as a function of absolute temperature. The first three columns are readings taken from smooth curves drawn through the experimentally determined points. The number of significant figures shows the internal consistency of the data and does not indicate the absolute value.

$T$ (°K)	$\frac{\rho V_1^2}{\frac{1}{2}(C_{11}+C_{12})+C_{44}}$	$\frac{\rho V_2^2}{C_{44}}$	$\frac{\rho V_3^2}{\frac{1}{2}(C_{11}-C_{12})}$	$C_{11}$	$C_{12}$	$\frac{B}{\frac{1}{3}(C_{11}+2C_{12})}$	$C_{12}-C_{44}$
0	5.3188	1.6313	1.6380	5.3255	2.0495	3.1415	0.4182
20	5.3188	1.6313	1.6380	5.3255	2.0495	3.1415	0.4182
40	5.3187	1.6313	1.6380	5.3254	2.0494	3.1414	0.4181
60	5.3187	1.6312	1.6379	5.3254	2.0496	3.1415	0.4184
80	5.3186	1.6312	1.6378	5.3252	2.0496	3.1415	0.4184
100	5.3181	1.6310	1.6368	5.3239	2.0503	3.1415	0.4193
120	5.3166	1.6298	1.6352	5.3220	2.0516	3.1417	0.4218
140	5.3138	1.6273	1.6315	5.3180	2.0550	3.1427	0.4277
160	5.3100	1.6238	1.6270	5.3132	2.0592	3.1439	0.4354
180	5.3036	1.6207	1.6220	5.3049	2.0609	3.1422	0.4402
200	5.2942	1.6178	1.6172	5.2936	2.0592	3.1373	0.4414
220	5.2846	1.6153	1.6124	5.2817	2.0569	3.1318	0.4413
240	5.2750	1.6130	1.6077	5.2697	2.0543	3.1261	0.4406
260	5.2653	1.6108	1.6031	5.2576	2.0514	3.1201	0.4406
280	5.2557	1.6089	1.5984	5.2452	2.0484	3.1140	0.4395
300	5.2462	1.6072	1.5937	5.2327	2.0453	3.1078	0.4381

## DISCUSSION OF RESULTS

The elastic behavior of a cubic crystal is completely specified by the two shear moduli,  $C=C_{44}$  and  $C'=\frac{1}{2}(C_{11}-C_{12})$  and the reciprocal compressibility or bulk modulus,  $B=\frac{1}{3}(C_{11}+2C_{12})$ .  $C$  is a measure of the resistance to shear deformation across the (100) plane in the [010] direction and  $C'$  is the resistance to shear deformation across the (110) plane in the  $[\bar{1}\bar{1}0]$  direction.  $B$  represents the resistance to deformation by a uniform hydrostatic pressure.

For tantalum the computed values of  $C$  and  $C'$  are shown plotted against temperature as the solid lines of Figs. 6 and 7. Figure 8 shows a corresponding solid line for  $B$ . These plots for  $C$  and  $C'$  show that these quantities vary with temperature in a manner similar to that observed for other metals. They approach 0°K with zero slope and depend linearly on temperature for a good portion of the temperature range. However,  $B$  as a function of temperature (Fig. 8) shows a de-

parture from previously observed behavior by displaying a positive slope up to about 100°K, then a slope reversal and negative slope up to room temperature.

In obtaining the elastic constants from a perturbation calculation, it would be expected that, if the anisotropy is not a strong function of temperature, the perturbation corrections would be small and of the same sign at all temperatures. Thus, if the experimental points decrease monotonically with increasing temperature as in Fig. 1, the elastic constants which only differ by small amounts from the experimental data should exhibit the same temperature dependence. That this is not the case for  $B$  is shown by the solid line in Fig. 8 which is plotted from the elastic constants listed in Table II. It is possible that a fortuitous choice of propagation direction, combined with the inevitable errors in angle and transit times, may lead to the observed behavior.

TABLE IV. The elastic constants of molybdenum, in units of  $10^{12}$  dyn-cm $^{-2}$ , as a function of absolute temperature. The first three columns are readings taken from smooth curves drawn through the experimentally determined points. The number of significant figures shows the internal consistency of the data and does not indicate the absolute value.

$T$ (°K)	$\frac{\rho V_1^2}{\frac{1}{2}(C_{11}+C_{12})+C_{44}}$	$\frac{\rho V_2^2}{C_{44}}$	$\frac{\rho V_3^2}{\frac{1}{2}(C_{11}-C_{12})}$	$C_{11}$	$C_{12}$	$\frac{B}{\frac{1}{3}(C_{11}+2C_{12})}$	$C_{12}-C_{44}$
0	4.3650	1.2503	1.3855	4.5002	1.7292	2.6529	0.4789
20	4.3639	1.2497	1.3855	4.4997	1.7287	2.6524	0.4790
40	4.3600	1.2488	1.3850	4.4962	1.7262	2.6495	0.4774
60	4.3557	1.2479	1.3840	4.4918	1.7238	2.6465	0.4759
80	4.3548	1.2468	1.3820	4.4900	1.7260	2.6473	0.4792
100	4.3495	1.2456	1.3807	4.4846	1.7232	2.6437	0.4776
120	4.3389	1.2446	1.3770	4.4713	1.7173	2.6353	0.4727
140	4.3292	1.2429	1.3719	4.4582	1.7144	2.6290	0.4715
160	4.3212	1.2402	1.3672	4.4482	1.7138	2.6253	0.4736
180	4.3160	1.2368	1.3662	4.4454	1.7130	2.6238	0.4762
200	4.3146	1.2333	1.3638	4.4451	1.7175	2.6267	0.4842
220	4.3127	1.2296	1.3595	4.4426	1.7236	2.6299	0.4940
240	4.3061	1.2257	1.3540	4.4344	1.7264	2.6291	0.5007
260	4.2988	1.2220	1.3487	4.4255	1.7281	2.6272	0.5061
280	4.2905	1.2188	1.3444	4.4161	1.7273	2.6236	0.5085
300	4.2825	1.2165	1.3417	4.4077	1.7243	2.6188	0.5078

In order to observe the effects of errors of measurement or orientation on the approximation method used in obtaining the elastic constants of tantalum, the input data were slightly changed and the elastic constants recalculated using a CDC 1604 computer. Thus, the measured values of  $\rho V^2$  were individually and collectively changed by  $\pm 1\%$ , the polar angles being held constant, or a measured polar angle  $\theta$  or  $\phi$  was changed by  $\pm 2^\circ$ , the values of  $\rho V^2$  and the other angle being held constant. The results of these calculations are indicated as dashed lines in Figs. 6-8 and show that for substantial input data changes the curves for  $C$ ,  $C'$ , and  $B$  are merely shifted up or down their respective ordinates with no changes in shape. Because there is no change of shape with these perturbations of the input data, it is concluded that the observed slope reversal effect in the bulk modulus curve for tantalum is a real effect.

In the tungsten crystal  $C$  and  $C'$  were measured directly since propagation was along [110]. These results are shown in Fig. 3. The variation of  $B$  with temperature has been calculated and is shown as the upper curve in Fig. 9.

The most striking feature of the variations of the measured quantities  $C$ ,  $C'$ , and  $\frac{1}{2}(C_{11}+C_{12})+C_{44}$  with temperature is their very flat behavior from liquid-air down to liquid-helium temperatures. This is the result of there being no observable difference in the elastic wave transit times for the three modes from liquid-air to liquid-helium temperatures. Because of this, the

bulk modulus  $B$  remains constant with increasing temperature out to approximately  $100^\circ\text{K}$ . Beyond this point,  $B$  displays a positive slope out to  $160^\circ\text{K}$  when it takes up a negative slope and a linear variation with temperature.

Figure 3 shows tungsten is nearly isotropic in shear in the temperature region measured, being exactly so at the crossover point between the two modes at about  $195^\circ\text{K}$ . Above  $140^\circ\text{K}$ , the shear modes vary quite linearly with temperature.

As was the case with tungsten,  $C$  and  $C'$  were measured directly for molybdenum. These results are displayed in Fig. 5, which shows that  $C$  varies monotonically with temperature but  $C'$  displays a tendency to level off in the  $90$  and  $180^\circ\text{K}$  regions.

The variation of  $B$  with temperature has been calculated and is shown as the lower curve in Fig. 9. It is seen that the slope of the bulk modulus curve goes from zero to negative as the temperature rises from  $0^\circ\text{K}$  but there are two subsequent pairs of gradual slope reversals over the remainder of the temperature range measured, one reversal at about  $80^\circ\text{K}$  and one at about  $230^\circ\text{K}$ . Reference to the  $1\%$  error flags in Figs. 5 and 9 readily establishes that these slope variations of  $C'$  and  $B$  all lie within about  $0.2\%$  of a line that would show monotonically decreasing behavior with temperature. However as Fig. 4 indicates, two separate measurements of the combination  $\frac{1}{2}(C_{11}+C_{12})+C_{44}$  vs temperature (the longitudinal acoustic mode for [110]) were made from liquid-air to room tempera-

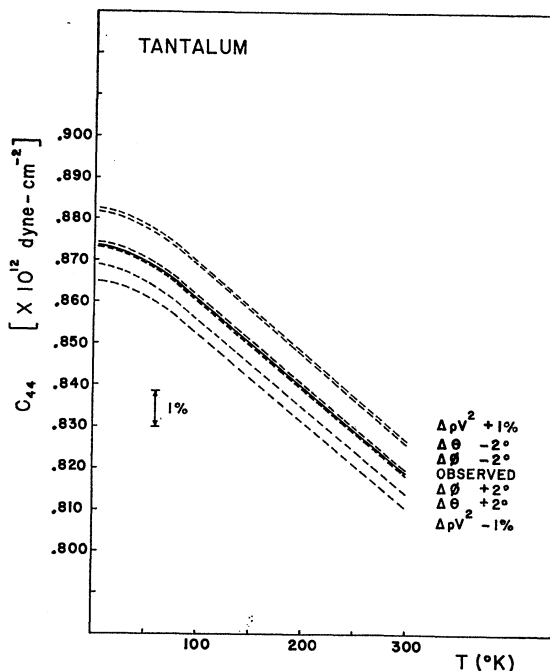


FIG. 6. The calculated shear constant  $C_{44}$  for tantalum as a function of temperature (solid line). The dashed lines show  $C_{44}$  vs  $T$  when  $\rho V^2$ ,  $\theta$ , or  $\phi$  are changed by the indicated amounts.

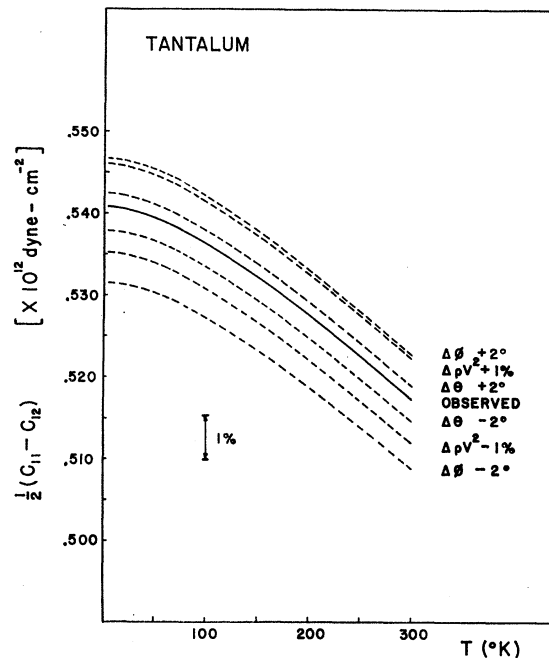


FIG. 7. The calculated shear constant  $\frac{1}{2}(C_{11}-C_{12})$  for tantalum as a function of temperature (solid line). The dashed lines show  $\frac{1}{2}(C_{11}-C_{12})$  vs  $T$  when  $\rho V^2$ ,  $\theta$ , or  $\phi$  are changed by the indicated amounts.

tures, with consistent results. This consistency indicates that the depicted rather than the monotonic behavior of  $B$  versus  $T$  is warranted.

It is seen from Figs. 1-5 that the temperature variation of the observed quantities is similar to that observed for other metals. That is, the elastic constants approach 0°K with zero slope and, except for molybdenum, are remarkably linear over a wide temperature range. The percentage change of the constants relative to their 0°K values is, with the exception of tantalum, about the same as that observed for the noble metals. Near room temperature all the constants vary linearly with temperature and have significantly smaller logarithmic derivatives than the noble metals. Unfortunately, the change of elastic constants with pressure have not yet been measured for these materials so that it is not possible to evaluate the intrinsic temperature dependence of the elastic constants.

Other investigators<sup>8,9</sup> have reported results for these metals obtained solely by dynamic methods. Also reported in the literature<sup>10,11</sup> are results obtained by dynamic measurement methods combined with Bridgman's compressibility data.<sup>12</sup>

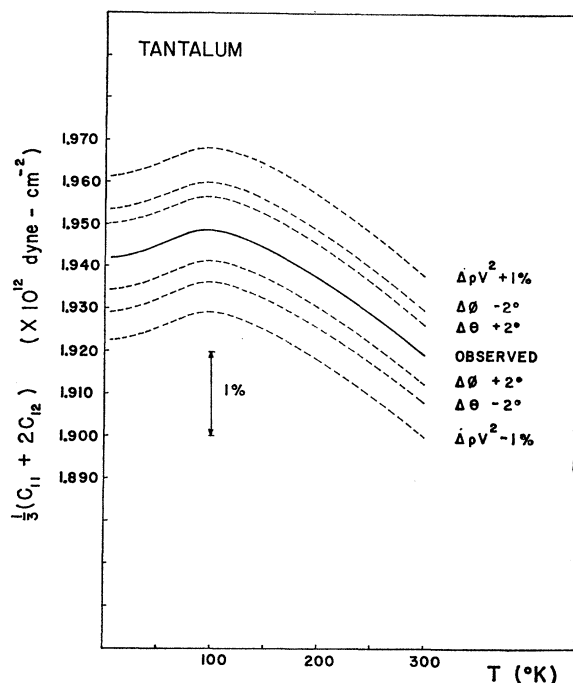


FIG. 8. The calculated bulk modulus,  $\frac{1}{3}(C_{11}+2C_{12})$ , for tantalum as a function of temperature (solid line). The dashed lines show  $\frac{1}{3}(C_{11}+2C_{12})$  vs  $T$  when  $\rho V^2$ ,  $\theta$ , or  $\phi$  are changed by the indicated amounts.

<sup>8</sup> D. I. Bolef, J. Appl. Phys. **32**, 100 (1961).

<sup>9</sup> D. I. Bolef and J. de Klerk, J. Appl. Phys. **33**, 2311 (1962).

<sup>10</sup> M. J. Druyvesteyn, Physica **8**, 439 (1941).

<sup>11</sup> S. J. Wright, Proc. Roy. Soc. (London) **A126**, 613 (1930).

<sup>12</sup> P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 329 (1925).

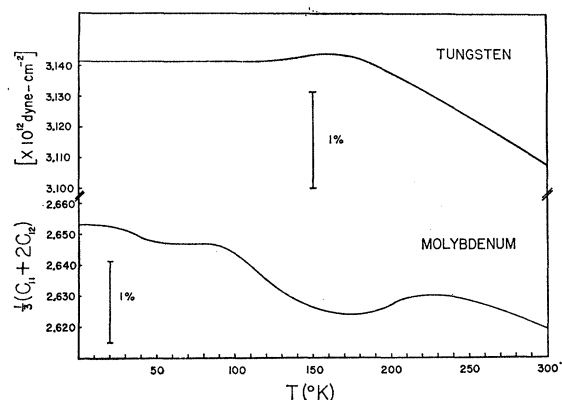


FIG. 9. The adiabatic bulk moduli  $\frac{1}{3}(C_{11}+2C_{12})$ , for tungsten and molybdenum as functions of temperature.

Table V compares room-temperature values from the literature with the results of this paper. The differences between the tantalum results reported by Bolef and by this paper tend to be close to the sum of the respective estimates of error ( $\sim 2\%$ ). This represents fair agreement. The tungsten reported by Bolef and de Klerk are in quite good agreement with those reported in this paper (within  $1\%$ ).

We note that for tungsten the difference between Bridgman's value of the compressibility and the result of this work is very close to the calculated difference between the room-temperature adiabatic and isothermal compressibilities. For tantalum and molybdenum, however, no such agreement is found, using either set of ultrasonically derived constants.

The difference in the values of the elastic shear constants reported for molybdenum by Bolef and de Klerk and by this paper are quite large. It seems clear, particularly in light of the agreement on tungsten, that these differences in moduli are real and that they depend on physical differences between the specimens rather than on differences in the measuring apparatus. That this must be the case is made more credible by considering that in measuring  $C_{44}$ , which is measured

TABLE V. The reported room temperature values of the adiabatic elastic constants of tantalum, tungsten, and molybdenum, in units of  $10^{12}$  dyn-cm<sup>-2</sup>.

Element	$C$	$C'$	$B$	Investigator
Tantalum	0.825	0.53	1.96	Bolef <sup>a</sup>
	0.818	0.518	1.919	This paper
Tungsten	1.51	1.51	2.99	Wright <sup>b</sup>
	1.53	1.54	3.08	Bridgman <sup>c</sup>
	1.604	1.598	3.083	Bolef & de Klerk <sup>d</sup>
	1.607	1.594	3.108	This paper
Molybdenum	1.09	1.4	2.73	Druyvesteyn <sup>e</sup>
	1.068	1.510	2.683	Bolef & de Klerk <sup>d</sup>
	1.216	1.342	2.619	This paper

<sup>a</sup> See reference 8.

<sup>b</sup> See reference 11.

<sup>c</sup> See reference 12.

<sup>d</sup> See reference 9.

<sup>e</sup> See reference 10.

directly for  $[110]$  propagation, the difference in the two reported values corresponds to a difference in transit time of  $0.5 \mu\text{sec}$  in the sample used, far outside the region of any reading error.

A possible explanation of the differences in reported room-temperature elastic constants ( $\sim 12\%$  differences for  $C$  and  $C'$  from the values of Bolef and de Klerk) for molybdenum is the influence of alloying of the impurities. Small amounts of a second phase have been found to change the single-crystal elastic constants of copper,<sup>13,14</sup> silver,<sup>15</sup> and lithium.<sup>16</sup> These changes in elastic constant have been interpreted in terms of changes in the long-range and short-range contributions to the elastic constants. The experiments indicate that the percent change in modulus per percent change in composition is seldom more than 4 and usually near unity. Since for molybdenum the observed percent change in modulus per percent change in composition is about 100, it is difficult to see how these differences can be interpreted on the basis of simple alloying.

Anelastic effects due to dislocations also contribute to changing the moduli. A dislocation contribution (diminution) to the moduli of about  $1\%$  has been observed for a single crystal of copper<sup>17</sup> and of lead<sup>18</sup> of purity in the 10 to 200 ppm range. In these experiments, the addition of small amounts of impurity tended to raise the observed modulus through dislocation pinning. Chambers and Schultz<sup>19</sup> have observed an internal friction spectrum for molybdenum in the low-temperature range that shows a pronounced peak in the region just below  $100^\circ\text{K}$  (the peak shifts with annealing) and a high-level minimum at about  $200^\circ\text{K}$ . They explain certain of the observed internal friction effects as being due to the interactions of gaseous interstitials and dislocations. The assay of the present molybdenum sample (Table I) shows a significantly higher gas content than the sample of Bolef and de Klerk. In addition, the present sample is much larger, and since dislocation densities increase rapidly with the diameter of the specimen,<sup>20</sup> conditions are right in the present sample for an anelastic mechanism such as that proposed by Chambers and Schultz to be quite pronounced.

The differences in the reported elastic shear constants for molybdenum are in opposite directions, and if these differences can be explained by means of an anelastic mechanism, then these differences should yield some evidence as to how dislocations are dis-

tributed in the lattice. Seeger<sup>21</sup> has conducted an analysis of low-temperature internal friction peaks wherein only a small fraction of the dislocations are considered to lie along crystallographic directions. The work of Thompson and Holmes<sup>22</sup> on copper indicates, however, that an appreciable fraction of the dislocations tend to lie along principal crystallographic directions. That the two orthogonal shear modes in the molybdenum sample are almost diametrically affected by this presumed dislocation-interstitial gas anelastic mechanism indicates that such a preferred alignment of dislocations may indeed be present.

### BULK MODULUS

As shown in Fig. 8, the bulk modulus of tantalum rises with increasing temperature above the  $4.2^\circ\text{K}$  value before beginning to decrease linearly. Observation of this anomalous behavior of  $B$  with temperature has led the authors to calculate the bulk moduli of the other transition elements whose elastic constants have been determined ultrasonically over the same temperature range. The following data were used: Alers<sup>23</sup> for vanadium; Rayne and Chandrasekhar<sup>24</sup> for iron; Alers, Neighbours, and Sato<sup>25</sup> for nickel; Rayne<sup>26</sup> for palladium; Carroll<sup>27</sup> for niobium; and this paper for tantalum, tungsten, and molybdenum. Curves presenting these results are shown in Figs. 10 and 11 where the bulk modulus has been normalized to its  $0^\circ\text{K}$  value, denoted by  $B_0$ . Figure 10 shows  $B/B_0$  versus temperature for the body-centered cubic transition metals. Here the behavior of niobium, tantalum, tungsten, and molybdenum is significantly different from that displayed by vanadium and iron. Similarly in the face-centered cubic elements shown in Fig. 11, palladium has quite a different temperature dependence from that displayed by nickel. Rayne<sup>26</sup> has ascribed the departure from linearity at temperatures above  $100^\circ\text{K}$  of the elastic constants of palladium to the change with temperature of the contribution to the elastic constants from the unfilled  $d$  band.  $B/B_0$  values from the elastic constants of copper,<sup>28</sup> silver, and gold<sup>1</sup> have been calculated and are included in Fig. 11 to indicate the temperature dependence of the bulk moduli of metals that have closed  $d$  shells.

Taking monotonically decreasing behavior with temperature as the norm, Figs. 10 and 11 show that the  $3d$  and closed  $d$  shell metals follow the norm. Niobium and palladium,  $4d$  metals, change the sign of their slope several times over the temperature range meas-

<sup>13</sup> G. Bradfield and H. Pursey, *Phil. Mag.* **44**, 437 (1953).

<sup>14</sup> J. R. Neighbours and Charles S. Smith, *Acta Met.* **2**, 591 (1954).

<sup>15</sup> R. Bacon and Charles S. Smith, *Acta Met.* **4**, 337 (1956).

<sup>16</sup> J. Trivisonno and Charles S. Smith, *Acta Met.* **9**, 1064 (1961).

<sup>17</sup> G. A. Alers and D. O. Thompson, *J. Appl. Phys.* **32**, 283 (1961).

<sup>18</sup> D. L. Waldorf and G. A. Alers, *J. Appl. Phys.* **33**, 3267 (1962).

<sup>19</sup> R. H. Chambers and J. Schultz, *Phys. Rev. Letters* **6**, 273 (1961).

<sup>20</sup> C. Elbaum, *J. Appl. Phys.* **31**, 1413 (1960).

<sup>21</sup> A. Seeger, *Phil. Mag.* **1**, 651 (1956).

<sup>22</sup> D. O. Thompson and D. K. Holmes, *J. Appl. Phys.* **30**, 525 (1959).

<sup>23</sup> G. A. Alers, *Phys. Rev.* **119**, 1532 (1960).

<sup>24</sup> J. A. Rayne and B. S. Chandrasekhar, *Phys. Rev.* **122**, 1714 (1961).

<sup>25</sup> G. A. Alers, J. R. Neighbours, and H. Sato, *J. Phys. Chem. Solids* **13**, 40 (1960).

<sup>26</sup> J. A. Rayne, *Phys. Rev.* **118**, 1545 (1960).

<sup>27</sup> K. J. Carroll, *Bull. Am. Phys. Soc.* **7**, 123 (1962).

<sup>28</sup> W. C. Overton and J. Gaffney, *Phys. Rev.* **98**, 969 (1955).



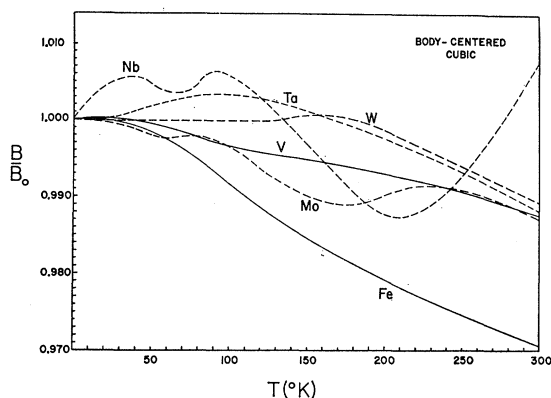


FIG. 10. The bulk moduli, normalized to their respective 0°K values, for certain of the body-centered cubic transition metals as functions of temperature. Solid lines are used for 3*d* metals, dashed lines for 4*d* and 5*d* metals.

ured, displaying a strong positive slope as room temperature is approached. Tantalum (5*d*) shows an early positive slope, then tends to follow the norm above 100°K. Tungsten (5*d*) has a flat response from 0°K out to 100°K where a positive slope finally asserts itself.  $B/B_0$  for tungsten then parallels that of tantalum very closely on up to room temperature. Molybdenum (4*d*) generally follows the norm but with undulating departures.

Figures 10 and 11 indicate a significant difference between the behavior of the bulk moduli of the 3*d* metals, and the 4*d*-5*d* metals. Such a difference is in consonance with the observance of ferromagnetism in the 3*d* group but not the 4*d*-5*d* groups.

One possible reason for this anomalous behavior of  $B$  with temperature that suggests itself is that these metals are involved in antiferromagnetic ordering in these temperature ranges, with associated anomalies in their thermal expansion coefficients. Evidence in support of this from other experiments is scarce and difficult to assess. Bolef, de Klerk, and Brandt<sup>29</sup> have reported anomalous thermal expansion behavior in the 180°K to 240°K region for vanadium. Figure 10, however, shows that vanadium is a well-behaved 3*d* metal in its  $B$  behavior. Hoare and Matthews<sup>30</sup> found a maximum in the magnetic susceptibility of palladium between 80 and 100°K, yet Crangle and Smith<sup>31</sup> recently looked for a specific-heat  $\lambda$  point in this region for palladium, with no success. They also measured the specific heat of vanadium, confirming the results of Clusius, Franzosini, and Piesbergen<sup>32</sup> that vanadium shows no anomaly between 175 and 265°K,

<sup>29</sup> D. I. Bolef, J. de Klerk, and G. B. Brandt, *Bull. Am. Phys. Soc.* **7**, 236 (1962).

<sup>30</sup> F. E. Hoare and J. C. Matthews, *Proc. Roy. Soc. (London)* **A212**, 137 (1952).

<sup>31</sup> J. Crangle and T. F. Smith, *Phys. Rev. Letters* **9**, 86 (1962).

<sup>32</sup> K. Clusius, P. Franzosini, and U. Piesbergen, *Z. Naturforsch.* **15a**, 728 (1960).

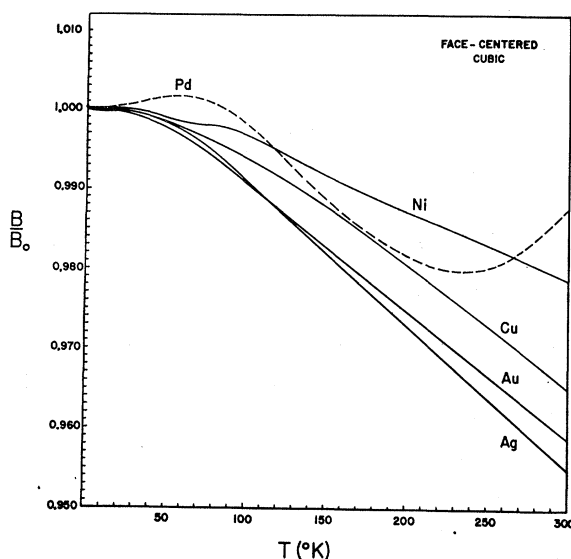


FIG. 11. The bulk moduli, normalized to their respective 0°K values, for certain of the face-centered cubic transition metals and for the noble metals.

the region in which Bolef *et al.* found anomalous thermal expansion behavior for the same metal. From the point of view that the body-centered cubic structure is the more natural vehicle for exhibiting antiferromagnetic behavior, and looking at the anomalous behavior of  $B/B_0$  versus  $T$  for the 4*d*-5*d* members of this group as possible evidence of this effect, it is then somewhat disconcerting that face-centered cubic palladium displays the same anomalous behavior. As the results of detailed specific heat, magnetic susceptibility, and thermal expansion for pure samples of these metals become available, the role of antiferromagnetic ordering in the transition metals may become clearer.

For body-centered and face-centered cubic structures, de Launay<sup>33</sup> has raised the possibility that  $C_{12}-C_{44}$  is equal to the bulk modulus of the electron gas of a metal. The temperature dependence of a free electron bulk modulus should show a steady decrease with increasing temperature as the lattice parameter increases. Reference to the  $C_{12}-C_{44}$  columns in Tables II, III, and IV shows that tantalum, tungsten, and molybdenum, like copper and silver, exhibit just the opposite effect, an increase of  $C_{12}-C_{44}$  with temperature. This reinforces de Launay's original admonition that the bulk modulus as derived from his considerations is a phenomenological quantity. It does not reflect on the validity of the Sommerfeld free electron model. However, correlation of  $C_{12}-C_{44}$  with the electronic bulk modulus of monovalent metals is still considered a possibility.<sup>34</sup>

<sup>33</sup> J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, pp. 276-284.

<sup>34</sup> W. C. Overton, *Phys. Rev.* **127**, 1107 (1962).

Excluded in the above calculations is the energy of the lowest state,  $W_0$ . Although its effect on the bulk modulus is usually taken to be small, it is possible that this may not be the case. Further consideration of this contribution await a cellular method calculation of  $W_0$ .

### OVERLAP FORCES

Fuchs<sup>35</sup> has accounted for the elastic constants of copper as being composed of two main parts: the electrostatic stiffnesses due to that part of the energy which can be regarded as the energy of an array of positive point charges immersed in a uniform negative sea; and the overlap energy due to the overlap of the charge distributions of ions plus the exchange energy. Following the lead of Fuchs and Zener,<sup>36</sup> Isenberg<sup>37</sup> has concluded that the major contribution to the elastic constants of the body-centered cubic transition metals is due to the overlap energy (the Coulomb interaction energy due to the overlap of the charge distribution of ions plus the exchange energy due to the same overlap).

The relations giving the overlap contributions to the elastic constants can be written<sup>8</sup> as:

$$\begin{aligned} N[rW_1']_1 &= \frac{3}{8}(C_{44}-C_{12}), \\ N[r^2W_1'']_1 &= \frac{3}{4}(C_{12}+2C_{44}), \\ N[r^2W_2'']_2 &= C_{11}-C_{44}, \end{aligned}$$

where  $N$  is the density of atoms,  $W_1$  is the nearest-neighbor interaction energy, and  $W_2$  is the next-nearest-neighbor interaction energy, and the primes represent differentiation. To a first approximation, the first derivative of  $W_2$  may be neglected,<sup>37</sup> and the remaining derivatives are evaluated at the nearest- or next-nearest-neighbor distance as appropriate. In applying the above formulas, only the part of the elastic constants due to overlap forces is included, i.e., the overlap contribution to the modulus is taken to be the observed modulus minus the contributions from all other sources.

Using the room temperature values of the elastic constants of tungsten as measured by Wright,<sup>11</sup> Isenberg determined that the second derivative of the next-nearest-neighbor interaction,  $W_2''$ , is positive, indicating a repulsive second-nearest-neighbor interaction in tungsten. The values he obtained for the first and second derivatives of the nearest-neighbor interaction  $W_1'$  and  $W_1''$  indicated a binding interaction for nearest neighbors. Isenberg interpreted these results as a possible substantiation of Zener's proposal<sup>36</sup> of an antiferromagnetic arrangement for the body-centered cubic transition elements vanadium, chromium, niobium, molybdenum, tantalum, and tungsten.

Taking the published values of the 0°K elastic con-

TABLE VI. Values of the derivatives of the nearest- and next-nearest-neighbor interaction energies attributable to overlap forces, as calculated from the 0°K elastic constants. Here  $N$  = the density of atoms,  $W_1$  = the nearest-neighbor interaction energy,  $W_2$  = the next-nearest-neighbor interaction energy, and the primes indicate differentiation with respect to  $r$ . The subscripts 1 and 2 outside the brackets indicate evaluation of the enclosed quantities at the nearest- and next-nearest-neighbor distances, respectively. The values given are in units of  $10^{11}$  dyn cm<sup>-2</sup>.

Element	$N[rW_1']_1$	$N[r^2W_1'']_1$	$N[r^2W_2'']_2$
Vanadium	-1.8	9.2	15.4
Niobium	-3.2	10.2	20.2
Tantalum	-2.1	20.5	15.9
Molybdenum	-1.0	26.2	29.9
Tungsten	-0.8	34.5	34.5
Iron	+0.8	20.2	7.8

stants of vanadium,<sup>23</sup> niobium,<sup>27</sup> and iron,<sup>24</sup> and the results of this paper, these same derivatives have been calculated. The results in units of  $10^{11}$  dyn cm<sup>-2</sup> are shown in Table VI. For all these transition elements except iron, the results are similar to Isenberg's. That is, the first derivative of the nearest-neighbor interaction energy is negative and the second derivatives of both interaction energies are positive.

The magnitude of the second derivatives generally increase as one passes down and to the right in the periodic table. The magnitude of the first derivative of  $W_1$  increases to the right in the periodic table. The derivatives for iron are different in sign and magnitude as might be expected for a ferromagnetic material.

We note that if a simple exponential form  $W_i = A_i e^{-\alpha_i r}$  is chosen for both  $W_1$  and  $W_2$ , then without neglecting  $W_2'$  it can be shown that

$$\begin{aligned} [(\alpha_2 r + \alpha_2^2 r^2)NW_2]_2 &= C_{11} - C_{44}, \\ [(\alpha_1 r + \alpha_1^2 r^2)NW_1]_1 &= (9/8)(C_{12} + C_{44}), \end{aligned}$$

where the subscript on the square bracket denotes the appropriate distance at which the quantity in the bracket is to be evaluated. The elastic constants used above are understood to include only that part due to overlap. For the transition metals considered here  $C_{11} > C_{44}$  and  $C_{12} > 0$  so that the above relations predict  $W_1$  and  $W_2$  both to be repulsive energies. This result is in agreement with ascribing the large cohesive energy of molybdenum and tungsten to the large number of electrons in the low-lying  $d$  band.<sup>38,39</sup>

### DEBYE TEMPERATURES

Using Houston's method as outlined by Betts, Bhatia, and Wyman,<sup>40</sup> the Debye temperatures of tantalum, tungsten, and molybdenum have been calculated from their 0°K elastic constants. Table VII presents these

<sup>35</sup> K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936).

<sup>36</sup> C. Zener, Phys. Rev. **81**, 440 (1951).

<sup>37</sup> I. Isenberg, Phys. Rev. **83**, 637 (1951).

<sup>38</sup> F. Seitz and R. P. Johnson, J. Appl. Phys. **8**, 186 (1937).  
<sup>39</sup> M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, 787 (1939).

<sup>40</sup> D. D. Betts, A. B. Bhatia, and Max Wyman, Phys. Rev. **104**, 37 (1956).

results and compares them with the results of calorimetric measurements. Although the values entered for the Debye temperatures of tantalum in Table VII differ by rather large amounts, the lattice specific heat given by  $\theta_0=261.9^\circ\text{K}$  is not in disagreement with the lower temperature part of the specific-heat data of White *et al.*<sup>41</sup> and Worley *et al.*<sup>42</sup> The data of Keesom and Desirant<sup>43</sup> are too scattered to admit critical comparison and Wolcott<sup>44</sup> lists only the value  $\theta_0=245^\circ\text{K}$ . Thus, the situation for comparison of elastic and calorimetric Debye temperatures of tantalum is similar to that for other metals<sup>45</sup>; i.e., where the calorimetric data are not too scattered, the lattice specific heat calculated from the elastic constants fits the low-temperature part of the calorimetric data.

Much the same remarks apply to tungsten and molybdenum. For tungsten, the data of Clusius and Franzosini<sup>46</sup> are fitted at the low-temperature end by  $\theta_0=384.3^\circ\text{K}$ . Clusius and Franzosini list  $\theta_0=380^\circ\text{K}$  and both Debye temperatures fit the data quite well.<sup>47</sup>

<sup>41</sup> D. White, C. Chou, and H. L. Johnston, *Phys. Rev.* **109**, 797 (1958).

<sup>42</sup> R. D. Worley, M. W. Zemansky, and H. A. Boorse, *Phys. Rev.* **99**, 447 (1955).

<sup>43</sup> W. H. Keesom and M. Desirant, *Physica* **8**, 273 (1941).

<sup>44</sup> N. M. Wolcott, in *Conférence de Physique des Basses Températures, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), Article 108.

<sup>45</sup> G. A. Alers and J. R. Neighbours, *Rev. Mod. Phys.* **31**, 675 (1959).

<sup>46</sup> K. Clusius and P. Franzosini, *Z. Naturforsch.* **14a**, 99 (1959).

<sup>47</sup> We are indebted to G. A. Alers for pointing out an error in our previously reported value for tungsten.

TABLE VII. The Debye temperatures of tantalum, tungsten, and molybdenum as calculated from the elastic constants and as derived from low-temperature specific-heat data.

Element	$\theta_0$	Reference
Tantalum	261.9	This work
	255	a
	246.5	b
	245	c
	231.0	d
Tungsten	384.3	This work
	380	e
	405	c
Molybdenum	474.2	This work
	470	c
	454	e
	445	f

<sup>a</sup> See reference 41.

<sup>b</sup> See reference 43.

<sup>c</sup> See reference 44.

<sup>d</sup> See reference 42.

<sup>e</sup> See reference 46.

<sup>f</sup> M. Horowitz and J. G. Daunt, *Phys. Rev.* **91**, 1099 (1953).

As in the case for tantalum, Wolcott lists only a number, and other data in the literature are too scattered for comparison.

For molybdenum, the calculated value  $\theta_0=474.2^\circ\text{K}$  gives a lattice specific heat in agreement with the lower temperature portion of the data of Clusius and Franzosini. The other published calorimetric data are not suitable for comparison.

#### ACKNOWLEDGMENT

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