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LATTICE VIBRATIONS OF TUNGSTEN*

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The frequency wave number dispersion relations of the lattice vibrations in the symmetric directions of body-centered cubic tungsten at room temperature have been measured by means of inelastic neutron scattering. The measurements were made with the Chalk River triple-axis crystal spectrometer using the constant $\underset{\sim}{Q}$ method.[1] The results in the three major directions [001], [110] and [111] are reported here together with a Born - Von Kármán general force model analysis from which is inferred the range and magnitude of the forces between the atoms in this metal. The connection between the results and the unusual elastic behavior of tungsten is discussed.

BECAUSE of the relatively high thermal neutron absorption cross-section (19.2 b.) and low coherent scattering cross-section (2.74 b.) of tungsten, four individual cylindrical single crystals (about 0.6 cm in diameter and 6.3 cm in length) were used as a composite specimen. The crystals were purchased from the Materials Research Corp. and were cut from a 25 cm length crystal having the $[1\bar{1}0]$ direction roughly along the cylindrical axis. In the experiment the four pieces of crystal were mounted vertically in an aluminum frame. The alignments of the crystals in the frame were individually adjusted. The relative alignment of the crystals is believed to have been within $1/4^{o}$. The frame was so arranged that either $(1\bar{1}0)$ or (001) planes of the crystals could be in the (horizontal) plane of the spectrometers. The [110] T_1 branch was measured in the (001) plane; the other branches in the $(1\bar{1}0)$ plane.

The results are shown in Fig. 1 (p. 74) where the frequencies (in units of 10^{12} c/s) are plotted against the component of the "reduced wave vector" $\vec{\zeta}$ defined by $\vec{q} = (2\pi/a)\vec{\zeta}$; for example, along the [110] direction $\vec{\zeta} = (\zeta\zeta 0)$. The frequencies of some modes at special points in reciprocal space are given in Table 1 (p. 74). The frequencies for the $L[\zeta\zeta 0]$ branch near the zone boundard are especially uncertain because the neutron groups for these phonons were poorly formed. The frequencies for $L[\zeta\zeta\zeta]$ with $\zeta = 0.6, 0.7, 0.8$ are also more than usually uncertain. The following general features of the curves should be noted:

1. The two transverse branches in the [001] and [111] directions are dengenerate by symmetry.
2. Zone boundary points in both [001] and [111] directions are equivalent and at these points all branches are degenerate by symmetry.
3. The longitudinal branch in the [001] direction has a maximum at about $\zeta = 0.7$. This implies a large second neighbour force constant α_2.
4. The two transverse branches in [110] direction are almost degenerate for small ζ and they cross at about $\zeta=0.45$. The small dip in the T_2 branch near $\zeta=0.45$ implies the existence of very long range forces.

The qualitative features of the measured dispersion curves can be understood however in terms of relatively short range general forces. A preliminary analysis of the curves using a Born - Von Kármán general force model[2] was carried out for forces of varying range, out as far as 8th neighbors. The results for the 3rd neighbor force model (seven force constants are plotted as broken

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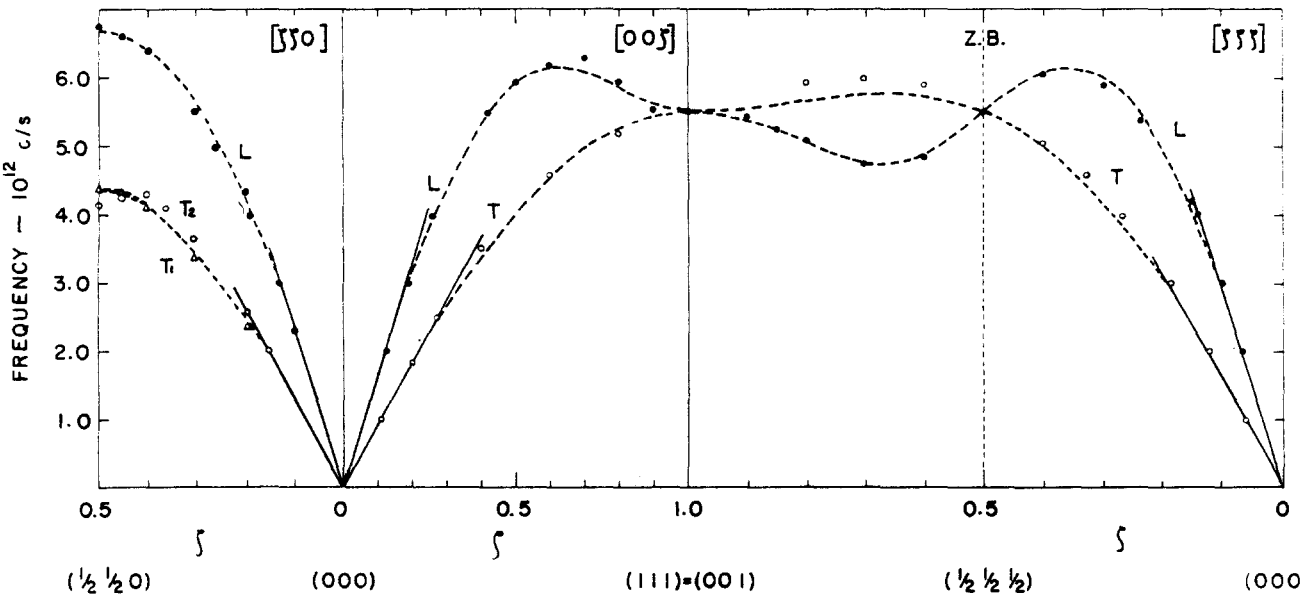

Dispersion curves for the lattice vibrations in the three major symmetric directions in tungsten at room temperature

TABLE 1

Frequencies of Phonons at Room Temperature at Some Specific Points in Reciprocal Space

Coordinate (in unit of $2\pi/a$) and mode ($a = 3.165$ Å)				Frequency (10^{12} c/s)
(0	0	1)	All modes degenerate	5.50 ± 0.1
(1/2	1/2	1/2)	L and T degenerate	5.50 ± 0.05
(1/2	1/2	0)L	Maximum point	6.75 ± 0.15*
(1/2	1/2	0)T_1		4.40 ± 0.05
(1/2	1/2	0)T_2		4.15 ± 0.05
(0	0	0.7)L		6.30 ± 0.07
(0.4	0.4	0)T_1		4.12 ± 0.03
(0.4	0.4	0)T_2		4.30 ± 0.05

*This value may possibly be in serious error because of poorly formed neutron groups.

TABLE 2

Stretching and Bending Force Constants in Units of 10^4 dynes/cm

Neighbors s	Stretching force constant $C_1(s) = \varphi''_s$	Bending force constant $C_B(s) = \varphi'_s/d_s$
1	$\alpha_1 + 2\beta_1 = 6.14$	$\alpha_1 - \beta_1 = 0.38$
2	$\alpha_2 = 4.73$	$\beta_2 = -0.08$
3	$\alpha_3 + \gamma_3 = 0.81$	$\beta_3 = -0.14$

lines in Fig. 1. The values of force constants thus obtained (in units of 10^4 dynes/cm and in the notation of reference 2) are as follows:

$$\alpha_1 = 2.30 \pm 0.02$$
$$\beta_1 = 1.92 \pm 0.03$$

$$\alpha_2 = 4.73 \pm 0.05$$
$$\beta_2 = -0.08 \pm 0.03$$

$$\alpha_3 = 0.32 \pm 0.01$$
$$\beta_3 = 0.14 \pm 0.02$$
$$\gamma_3 = 0.49 \pm 0.02$$

It is seen that the qualitative features of the curves are reproduced in this model. Taking into account additional neighbors up to 6th (15 force constants) does not improve the agreement significantly. If atoms up to 8th neighbors are included, the agreement becomes better, although the hump in the $[110]T_2$ branch near the zone boundary still cannot be reproduced. Thus it must be concluded that the detailed nature of the forces is quite complicated in tungsten in that, besides the strong short range forces, there exists a weak but long range force system analogous to, but weaker than, that found for niobium by Nakagawa et al.[3] A few qualitative conclusions can be based on the 3rd neighbor force model:

1. According to the recent measurement of adiabatic elastic constants of tungsten by Featherston and Neighbours,[4] the condition of isotropy, i.e., $C_{44} = 1/2\ (C_{11} - C_{12})$, is satisfied to within 1% in the temperature range from 0°K to 300°K. Physically, C_{44} and $1/2\ (C_{11} - C_{12})$ are two shear moduli and their equality implies that the two mutually perpendicular shear elastic waves (for an direction of propagation) have the same velocity. This fact has the special consequence that the slopes of $[110]T_1$ and $[110]T_2$ are the same in the long wave length limit ($\zeta = 0$). This is clearly seen also in our experimental results. In fact, we have tested the consistency of our results in the long wave length limit with the elastic constants by imposing or not imposing the condition that the slopes of the dispersion curves must approach the correct sound velocities given by the elastic constants; the two sets of force constants so obtained agreed within the experimental errors. By the method of long waves,[5] it can be shown that the elastic constants are related to the force constants by the relations (up to 3rd neighbors):

$$aC_{11} = 2\alpha_1 + 2\alpha_2 + 8\alpha_3$$

$$aC_{44} = 2\alpha_1 + 2\beta_2 + 4\alpha_3 + 4\beta_3$$

$$a(C_{11}-C_{12})/2 = 2\alpha_1 - 2\beta_1 + \alpha_2 + \beta_2 + 6\alpha_3 + 2\beta_3 - 4\gamma_3$$

Thus, the condition of isotropy imposes the condition upon these force constants that the combination $2\beta_1 - \alpha_2 + \beta_2 - 2\alpha_3 + 2\beta_3 + 4\gamma_3 = 0$. This condition is approximately satisfied by our values of force constants (the combination = 0.08). For forces extending only to 2nd neighbor, it can be shown easily the $[110]T_1$ and $[110]T_2$ should be degenerate all the way to the zone boundary; this is not the case and consequently the forces must extend beyond 2nd neighbors.

2. In order to discuss the nature of the interaction between the atoms let us adopt the central force model, i.e., assume that the interation is binary and that it can be derived

from an effective potential depending only on the distances between atoms. The condition of validity of this model is the Cauchy relation $C_{12} = C_{44}$, which is satisfied to within 22% according to the reported values of elastic constants[4], or equivalently the Born-Huang equilibrium condition[5, 2] that the combination $\alpha_1 - \beta_1 + \beta_2 + 4\beta_3 = 0$, which is satisfied approximately (experimentally the combination= -0.26). In such a model the force constants can be related[5] to linear combinations of first and second derivatives of the effective potential function ψ_s, where s denotes different neighbors. If we take linear combinations of force constants in such a way that they are proportional to ψ_s' and ψ_s'' respectively, we get the result in Table 2, where d_s is the equilibrium distance to the neighbors s. The combinations of force constants which are proportional to ψ_s'' and ψ_s' can be interpreted[6] as bond-stretching ($C_1(s)$) and bond-bending ($C_B(s)$) force constants respectively. Assuming the same functional form for the potentials of all neighbors s, it is clear from the relative signs of $C_1(s)$ and $C_B(s)$ in Table 2 that it is quite impossible to construct a sensible potential function between atoms, whereas for sodium, it was found possible[7] to do so. However, if the functional form of the ψ_s is different for different neighbors, then the signs of $C_1(s)$ and $C_B(s)$ suggest that the force between an atom and its first neighbor is attractive and the forces between it and its second and third neighbors are probably repulsive, in agreement with conclusions reached by Isenberg[8], and by Featherston & Neighbours[4], from consideration of the elastic constants.

We have also calculated the frequency distribution function using the 23 force constants obtained from the 8th neighbor best fit. The frequency distribution curve shows two pronounced peaks, at 4.6×10^{12} and at 6.3×10^{12} c/sec. The Debye temperature $\theta_D(T)$ calculated from this frequency distribution function is 380°K at absolute zero; it gradually decreases through values θ_D + 363°K at T = 20°K and 318°K at 50°K to an essentially constant value, θ_D = 312°K, for temperatures from 100°K to 300°K.

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On a mesuré les courbes de dispersion des fréquences des oscillations thermiques se propageant suivant les axes de symétrie du tungstè avec la spectroscopie neutronique. Les resultats (analysés selon la théorie Born-Von Kármán) se montrent que les forces interatomiques s'étendent au déla les 8-e voisins. Cependant, les voisins 1-r et 2-e les contributions principales aux forces; celles-ci sont, respectifment, attrayantes et repoussantes.