

various angles of incidence, all taken in the vicinity of a Kiessig minimum. Each profile represents a change of incident angle of 4 sec of arc over its predecessor. The dip, as expected, is seen to move across the profile. The low-angle side of the profile is distorted because of the sharp rise in the reflection coefficient at the lower angles.

Since the experimental reflection curve is distorted and smoothed out by surface imperfections and a wide counter window, it is difficult to show experimentally that the curves in Fig. 5 are actual mathematical folds of the incident beams' angular profile with the reflection curve. A semiquantitative demonstration could be made by folding an experimentally determined incident profile with a theoretically calculated reflection curve. The main difficulty encountered in such a procedure is that the incident beam reflected at an angle less than the critical angle intersects so much of the surface of the film, that the surface ripples widen the profile of the reflection considerably. The assumption may be made

that the beam which is totally reflected from the film has the proper shape but should be narrowed so that its half-width is in agreement with the average half-width of the experimental profiles of Fig. 5. This resulting curve may be assumed to be a good approximation to the profile of the incident beam to be used.

Figure 6 shows the calculated reflection curve near the 8th Kiessig maximum. The curve was calculated using Parratt's general equation for a three-media model.¹ The absorption coefficient used was assumed to be the same as the linear absorption coefficient. The same figure shows the assumed incident beam profile and a sample fold of the assumed incident beam profile with the calculated reflection curve. Figure 7 shows a series of such folds made at 5-sec intervals. The general trend of the dip is clearly evident and the peak shapes are seen to resemble those of Fig. 5 which shows the observed reflected profiles for several angles of incidence.

Lattice Dynamics and Specific Heats of Some Transition Metals on Krebs's Model

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Krebs's model for the lattice dynamics of cubic metals has been extended by including the third-nearest-neighbor ionic interactions. The cases of three transition metals, viz., α -iron, molybdenum and tungsten, are discussed in this paper. The force constants appearing in the secular equations for the lattice frequencies are estimated from experimental elastic constants and one observed vibration frequency. The phonon dispersion curves for the three major symmetry directions show a good agreement with the results for neutron scattering. The frequency distributions are computed. The theoretical specific heats and Debye parameters also exhibit a good agreement with the experimental data.

I. INTRODUCTION

WHILE considerable work has been done on the lattice dynamics of monovalent cubic metals, very little attention has been paid so far to those belonging to the transition class. The transition elements present several features of great theoretical interest. In these elements, the un-ionized free atom contains an incomplete d shell of lower principal quantum number than the outer s shell. The methods of soft-x-ray spectroscopy have established that in the crystals of these elements, the ns , np , and $(n-1)d$ electron states of the free atom have broadened into overlapping bands so that the electrons concerned are in the hybrid (spd) states. This gives rise to allotropy and multiple chemical valencies and introduces complexities in the theoretical studies of these metals. Recent work^{1,2} on

the phonon dispersion relations from the momentum and energy changes in the inelastic scattering of slow neutrons has, however, stimulated fresh interest in the study of lattice dynamics of these complicated atoms.

The phonon frequency distribution function of a solid can be computed from the Born-von Karman³ theory of lattice vibrations if the interatomic force constants are known. The lattice dynamics of a bcc crystal assuming central forces between the nearest and next nearest neighbors has been discussed by various workers.⁴⁻⁹ All these models have, however, one common drawback: The frequencies computed from them are not periodic in reciprocal space. This has been empha-

³ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956), Chap. II.

⁴ P. C. Fine, *Phys. Rev.* **56**, 355 (1939).

⁵ B. Dayal, *Proc. Indian Acad. Sci.* **A20**, 24 (1944).

⁶ J. de Launay, *J. Chem. Phys.* **21**, 1975 (1953); *Solid State Physics* (Academic Press Inc., New York, 1956), Vol. 2, p. 220.

⁷ E. Bauer, *Phys. Rev.* **92**, 58 (1953).

⁸ A. B. Bhatia, *Phys. Rev.* **97**, 363 (1955).

⁹ P. K. Sharma and S. K. Joshi, *J. Chem. Phys.* **39**, 2633 (1963).

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¹ S. H. Chen and B. N. Brockhouse, *Solid State Commun.* **2**, 3 (1964); **2**, 73 (1964).

² A. D. B. Woods and S. H. Chen, *Solid State Commun.* **2**, 8 (1964); **2**, 233 (1964).

sized by Lax,¹⁰ who has discussed the general principles of a model in which these requirements are satisfied by the inclusion of umklapp processes. Krebs¹¹ gave a practical shape to Lax's ideas. In this model, the contribution of the ions to the elements of the dynamical matrix is exactly the same as in the de Launay model. The electronic contribution, however, is different. The frequencies computed by Krebs for the three major symmetry directions in the case of sodium agree well with the experimental neutron scattering data. In an earlier paper,¹² hereinafter referred to as I, the present authors tried Krebs's model on the other alkali metals and a good agreement was found between the theory and experimental data on heat capacities. A similar good agreement has been reported from this laboratory by Shukla and Dayal¹³ in case of noble metals.

In Krebs's theory, when calculating the electronic term, one requires the value of effective ionic charge Z . For alkali metals Z was taken to be unity throughout—an assumption which is justified by the fact that in these metals there is a solitary electron outside a very stable electron configuration surrounding each nucleus. In transition metals, the problem of finding the effective number of free electrons per atom is not so simple. The three metals discussed in this paper, viz., α -Fe, Mo, and W, have the electron configurations $3d^64s^2$, $4d^55s$, and $5d^46s^2$, respectively, outside the core of closed shells. There have been some energy-band calculations for these metals, the most extensive being for iron.^{14–21} It is difficult to correlate the results of these workers because of the nature of, and the many differences in, the approximations and assumptions made by them. Callaway²² has shown, however, that in the case of this metal there must be less than two "s electrons" per atom. The value of 1.8 has been found to be most appropriate in our study. The position regarding Mo and W is not so clear. However, Morin and Maita²³ and Manning and Chodorow²⁴ have discussed the density of states and electronic specific heats in the cases of Mo and W, respectively. From the low values of $N(E)$ for

the d bands of these two metals²⁵ one can only infer that there are roughly two "s electrons" per atom—a conclusion which is supported by the values quoted by Jorgenson²⁶ and Semenchenko²⁷ from other studies.

The earlier computations of Fine⁴ and Dayal⁵ for W, of Sharan²⁸ for Mo and W, of Clark²⁹ for α -Fe, Mo, and W, and of Sharan and Tiwari³⁰ for α -Fe do not show a good agreement with the experimental data for lattice specific heats at low temperatures. This is not surprising because in these metals, the magnitude of the second-neighbor force constant comes out to be of the same order as that for first neighbors. This suggests that the third-neighbor force constant is not negligible. This is found by Curien³¹ also, who has taken into consideration both central and noncentral forces up to the third neighbors and has estimated the force constants for α -Fe from the diffuse x-ray scattering measurements.

In view of the success of Krebs's model in other metals^{12,13} we felt that it was desirable to apply this model to these three transition metals, namely α -Fe, Mo, and W, after including the third-neighbor central-force interaction between the ions. This has led to a good agreement between the theoretical and experimental data obtained from neutron scattering and specific heats. The results are presented in this paper.

II. SECULAR DETERMINANT

Proceeding in the usual way, the secular determinant for the determination of circular frequencies ω may be written as

$$|M_{ij} - m\omega^2 I| = 0, \quad (1)$$

where $i, j = 1, 2, 3$. I is the unit matrix of the order three and m is the mass of the atom. The element of the dynamical matrix, M_{ij} , can be expressed as the sum of two coupling coefficients: A_{ij} , due to ion-ion interactions, and I_{ij} , due to electron-ion interactions.

As mentioned earlier, Krebs¹¹ has considered the ionic interactions between the first and second neighbors alone on lines similar to de Launay.⁶ In a bcc crystal there are 12 third neighbors having position coordinates $R_0(\pm 1, \pm 1, 0)$, $R_0(\pm 1, 0, \pm 1)$, and $R_0(0, \pm 1, \pm 1)$, where R_0 is half the lattice constant. Suppose α_1 , α_2 , and α_3 represent the atomic force constants corresponding to the first, second, and third neighbors, respectively, when we assume the interatomic forces to be central. The coupling coefficients A_{ij} can be easily

²⁵ J. G. Daunt, in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. I, Chap. XI.

²⁶ C. K. Jorgenson, *Orbitals in Atoms and Molecules* (Academic Press Inc., New York, 1962), Chap. VII.

²⁷ V. K. Semenchenko, *Surface Phenomenon in Metals and Alloys* (Pergamon Press, Inc., New York, 1962), Appendices.

²⁸ B. Sharan, *Phys. Status Solidi* **1**, 243 (1961).

²⁹ C. B. Clark, *Phys. Rev.* **125**, 6 (1962); **125**, 1898 (1962).

³⁰ B. Sharan and L. M. Tiwari, *Phys. Status Solidi* **3**, 1408 (1963).

³¹ H. Curien, *Bull. Soc. Franc. Mineral. Crist.* **75**, 197 (1952); *Acta Cryst.* **5**, 393 (1952).

¹⁰ M. Lax, *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press, Inc., New York, 1964), p. 179.

¹¹ K. Krebs, *Phys. Letters* **10**, 12 (1964); *Phys. Rev.* **138**, A143 (1965).

¹² P. S. Mahesh and B. Dayal, *Phys. Status Solidi* **9**, 351 (1965).

¹³ M. M. Shukla and B. Dayal, *Phys. Status Solidi* **8**, 475 (1965); *J. Phys. Chem. Solids* **26**, 1343 (1965).

¹⁴ M. F. Manning, *Phys. Rev.* **63**, 190 (1943).

¹⁵ J. C. Slater, *Rev. Mod. Phys.* **25**, 199 (1953).

¹⁶ J. Callaway, *Phys. Rev.* **99**, 500 (1955).

¹⁷ F. Stern, *Phys. Rev.* **116**, 1399 (1959).

¹⁸ E. F. Belding, *Phil. Mag.* **8**, 4 (1959); **8**, 1145 (1959).

¹⁹ J. H. Wood, *Phys. Rev.* **117**, 714 (1960).

²⁰ L. F. Mattheiss, *Phys. Rev.* **134**, A970 (1964).

²¹ N. F. Mott, *Advan. Phys.* **13**, 51 (1964); **13**, 325 (1964).

²² J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964), Chap. III.

²³ F. J. Morin and J. P. Maita, *Phys. Rev.* **129**, 3 (1963); **129**, 1115 (1963).

²⁴ M. F. Manning and M. I. Chodorow, *Phys. Rev.* **56**, 787 (1939).

derived in terms of these force constants. The typical diagonal and nondiagonal coupling coefficients are

$$A_{11} = (8/3)\alpha_1(1 - c_1c_2c_3) + 4\alpha_2s_1^2 + 4\alpha_3(2s_1^2 + s_2^2 + s_3^2 - 2s_1^2s_2^2 - 2s_1^2s_3^2),$$

$$A_{12} = (8/3)\alpha_1(s_1s_2c_3) + 8\alpha_3(s_1s_2c_1c_2),$$

where $c_i = \cos 2\pi k_i R_0$ and $s_i = \sin 2\pi k_i R_0$. Here $2\pi k_i$ are the components of the phonon wave vector $2\pi \mathbf{k}$ ($k = 1/\lambda$). In the limits of very long waves (small k), Eq. (1) must be identical with the Christoffel equation of elasticity. The required relations between the interatomic force constants and the elastic constants have been obtained by expanding the elements A_{ij} for the three directions [100], [110], and [111] in powers of k_i , retaining only quadratic terms, and comparing the results with the elastic secular equation. As in Krebs's model, we have assumed that $C_{12} - C_{44}$ represents the bulk modulus of the electron gas and have calculated the ionic force constants from the elastic constants ($C_{11} - C_{12}$) and C_{44} . As the number of parameters to be determined is three, an additional relation is obtained with the help of the experimentally observed frequency at the Brillouin zone boundary in the [111] direction. The numerical value of this frequency has been quoted in Table I.

Krebs has considered a screened Coulomb interaction between metal ions surrounded by electrons with Bloch-type functions. The electronic coupling coefficients I_{ij} for a monovalent metal have been given in paper I. In polyvalent metals, the number of electrons is not equal to the number of atoms and, therefore, the interelectronic distance r_e is not equal to r_s but is given by the relation (Raimes³²)

$$r_e = Z^{-1/3} r_s.$$

All the expressions for I_{ij} in Paper I which involve r_s consequently get modified on account of the effective ionic charge Z .

In Paper I, it was found that the value of the screening parameter shows a gradual transition from the Bohm-Pines value to the Thomas-Fermi one as the ionic size increases. For the three metals under consideration in this work, the ionic sizes are very small and, therefore, the Bohm-Pines value of the screening parameter³³ has been used in the computations.

III. NUMERICAL COMPUTATIONS

The calculation of the frequency spectrum has been performed by a numerical sampling of the frequencies for a discrete subdivision of the wave-vector space. The first Brillouin zone is divided in an evenly spaced sample of 1000 wave vectors. From the symmetry requirements

³² S. Raimes, *The Wave Mechanics of the Electrons in Metals* (North-Holland Publishing Company, Amsterdam, 1961), Chap. VII.

³³ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1963), Chap. IV.

TABLE I. Constants for the three metals.

Element	Elastic constants (10^{12} dyn/cm ²)			$\nu(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (10^{12} sec ⁻¹)
	C_{11}	C_{12}	C_{44}	
α -Fe	(a)	2.3310	1.3544	1.1783
	(b)	2.2800	1.3200	1.1650
Mo		4.4077	1.7243	1.2165
W		5.2327	2.0453	1.6072

^a Rayne and Chandrashekhar (Ref. 35).

^b Lord and Beshers (Ref. 36).

these 1000 points are reduced to only 46 nonequivalent points³⁴ besides the origin, lying within 1/48 part of the Brillouin zone which is irreducible under the symmetry operations that leave the roots of the secular determinant unchanged. The calculation of the frequencies has been made for these nonequivalent points by means of Eq. (1).

The numerical values of the elastic constants and the frequency ν at the zone boundary appearing in the text are given in Table I.

The c_{ij} for the three metals correspond to 300°K. In the case of α -Fe, (a) and (b) refer to the experimental data from Rayne and Chandrashekhar³⁵ and Lord and Beshers,³⁶ respectively. For Mo and W, the c_{ij} are from Featherston and Neighbours.³⁷ The values for mass and lattice constant have been taken from *International Tables for X-ray Crystallography*, Vol. III (1962). The values of frequency ν are from the work of Low,³⁸ Woods and Chen,² and Chen and Brockhouse¹ in the cases of α -Fe, Mo, and W, respectively.

The values of the force constants for the first, second, and third neighbors, obtained with the help of above input data, are given in Table II.

The dispersion curves for the lattice vibrations in the three major symmetry directions in α -Fe,³⁹ Mo, and W at room temperature are shown in Figs. 1, 2, and 3,

TABLE II. Force constants in 10^4 dyn cm⁻¹.

Neighbor	Force constants	α -Fe		Mo	W
		(a)	(b)		
1st	α_1	5.535	5.649	4.269	6.619
2nd	α_2	1.556	1.589	3.731	4.707
3rd	α_3	-0.234	-0.320	0.737	0.505

³⁴ B. Dayal and B. Sharan, Proc. Roy. Soc. (London) **A259**, 361 (1960).

³⁵ J. A. Rayne and B. S. Chandrashekhar, Phys. Rev. **122**, 6 (1961); **122**, 1715 (1961).

³⁶ A. E. Lord, Jr., and D. N. Beshers, J. Appl. Phys. **36**, 5 (1965); **36**, 1620 (1965).

³⁷ F. H. Featherston and J. R. Neighbours, Phys. Rev. **130**, 4 (1963); **130**, 1324 (1963).

³⁸ G. E. Low, Proc. Phys. Soc. (London) **79**, 479 (1962).

³⁹ As the difference between the computed frequencies from (a) and (b) data for elastic constants are not appreciable, the dispersion curves in Fig. 1 and the frequency-distribution curve in Fig. 4 refer to data (a) only.

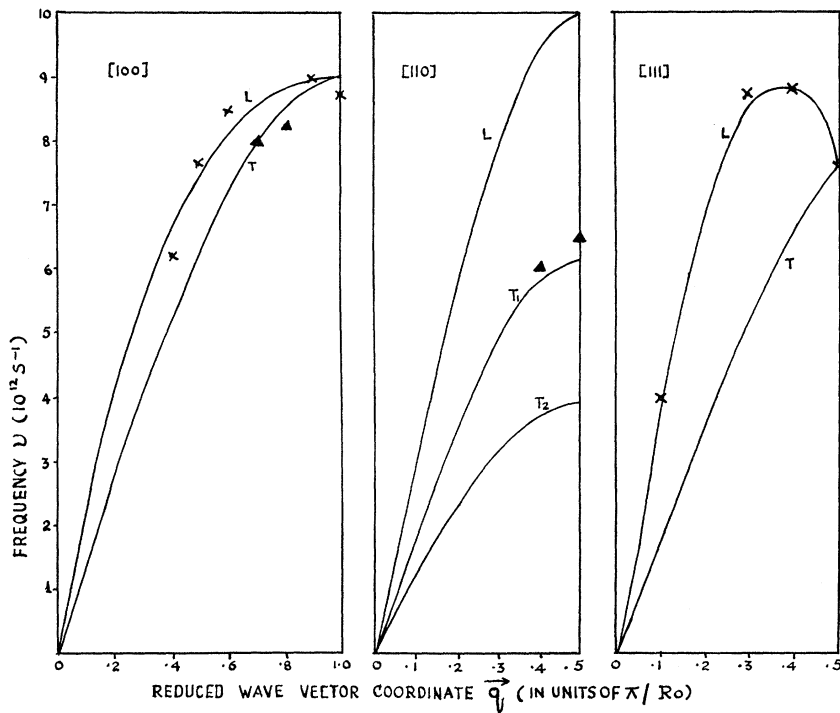


FIG. 1. Dispersion curves for α iron. Experimental data of Low (Ref. 38) are marked as X and \blacktriangle for the longitudinal and transverse branches, respectively.

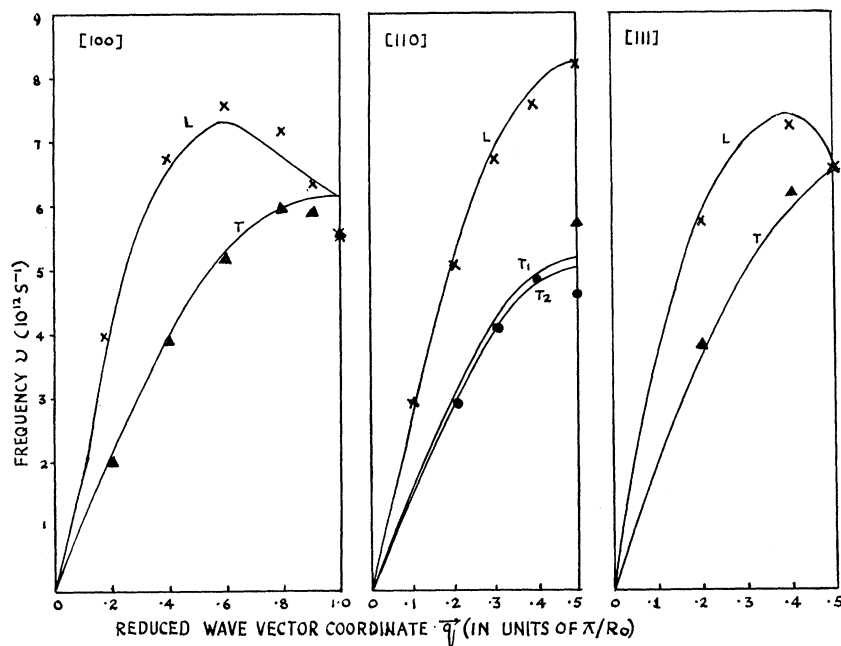


FIG. 2. Dispersion curves for molybdenum. Experimental data of Woods and Chen (Ref. 2) are marked as X, \blacktriangle , and \bullet for the longitudinal and the first and second transverse branches, respectively.

respectively. In these figures the frequencies ν ($=\omega/2\pi$) have been plotted against the reduced wave-vector coordinate in units of π/R_0 . The experimental points are also shown for comparison.

As the values of the frequencies corresponding to all the chosen wave vectors are too numerous to be tabulated in this paper, we have constructed frequency dis-

tribution functions $G(\nu)$ for the three metals. By definition, the number of normal modes with frequencies lying between ν and $\nu+\Delta\nu$ is given by $G(\nu)\Delta\nu$. The entire frequency range is divided into a number of intervals (marked in the figures) and each frequency has been weighted properly. Smooth curves fitted into the histograms for the three metals have been shown in

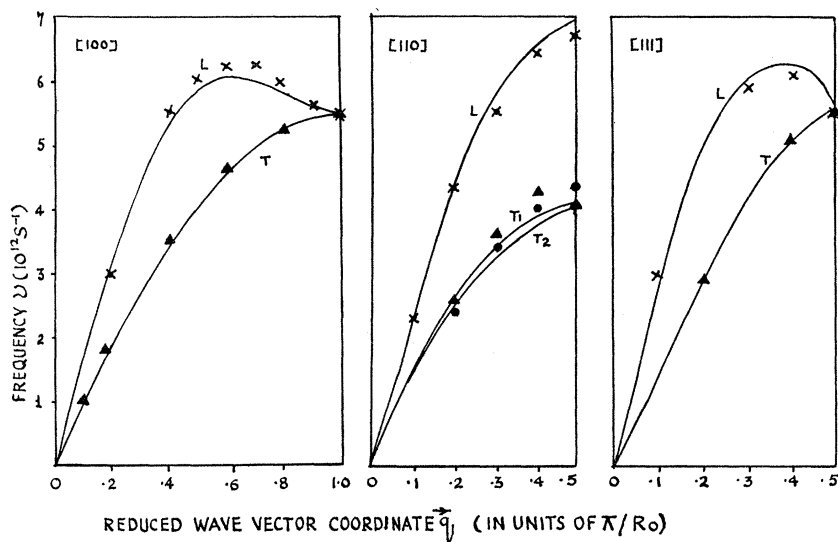


FIG. 3. Dispersion curves for tungsten. Experimental data of Chen and Brockhouse (Ref. 1) are marked as X, \blacktriangle , and \bullet for the longitudinal and the first and second transverse branches, respectively.

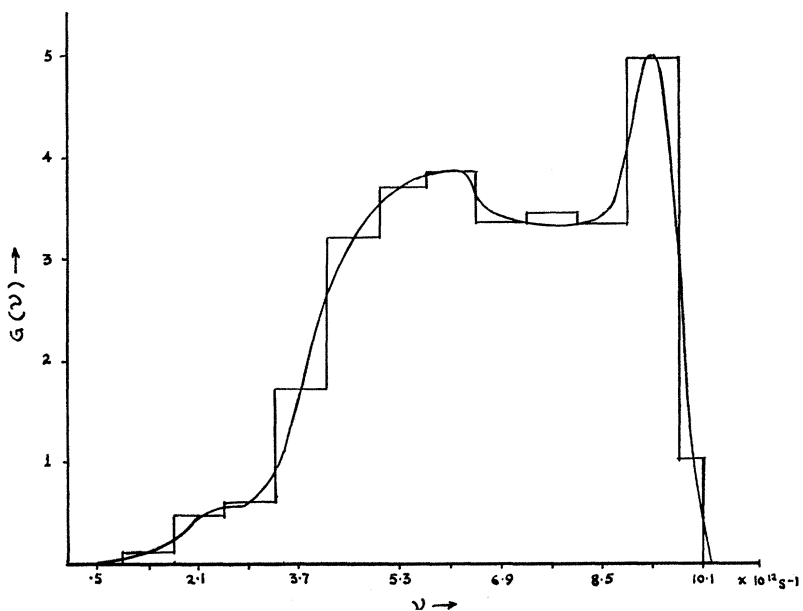


FIG. 4. The vibrational-frequency distribution function versus frequency curves for alpha iron.

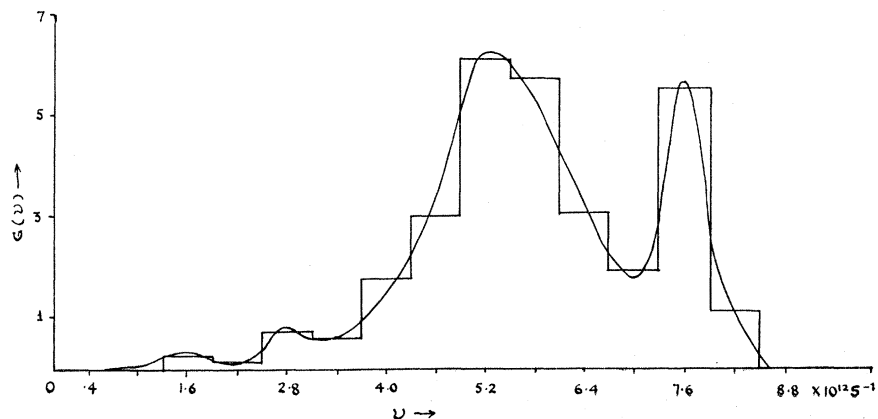


FIG. 5. The vibrational-frequency distribution function versus frequency curves for molybdenum.

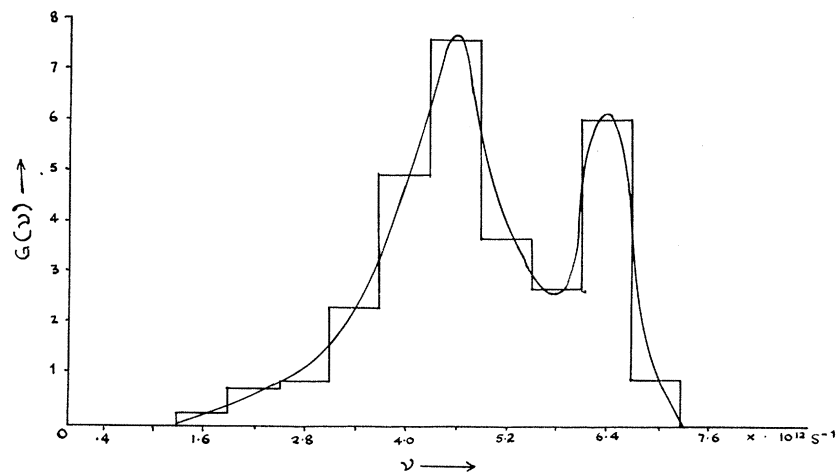


FIG. 6. The vibrational-frequency distribution function versus frequency curves for tungsten.

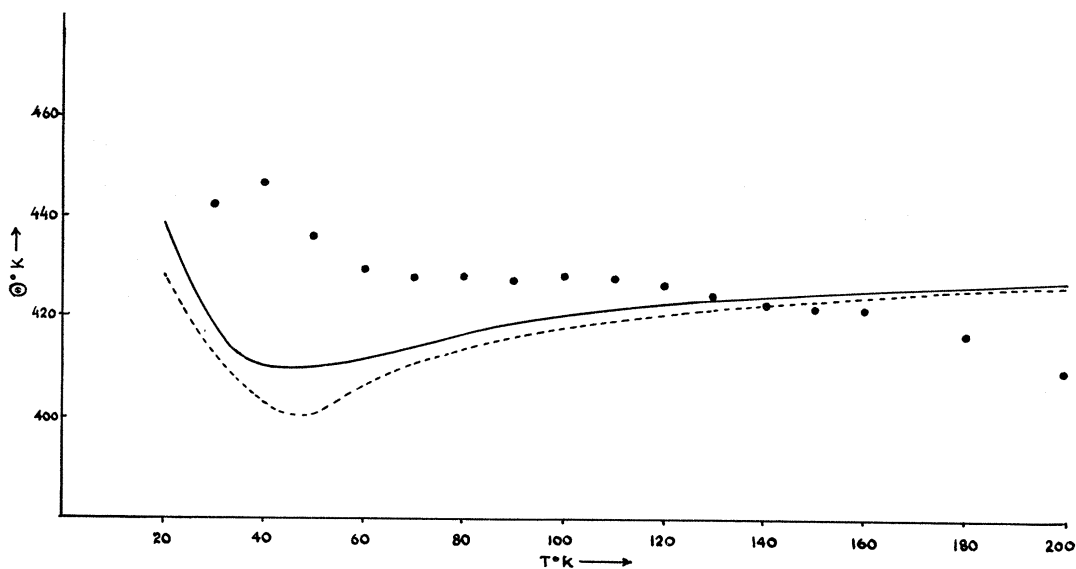


FIG. 7. Θ - T curves for α iron. Experimental data for Duyckaerts (Ref. 41) and Kelley (Ref. 42) are marked as \bullet .

Figs. 4, 5, and 6. The curves have not been normalized and the units of $G(\nu)$ are arbitrary.

The specific heats at constant volume have been calculated by adopting Blackman's sampling technique. For this purpose, the frequencies have been divided into intervals of $0.2 \times 10^{12} \text{ sec}^{-1}$. The specific heats have been evaluated from Einstein's functions corresponding to the midpoint of each interval and the values of C_v (lattice) computed as well as observed are listed in Table III for the three metals. The theoretical Θ - T curves for these metals are shown in Figs. 7, 8, and 9 where they have been compared with experimental data. At very low temperatures, this mesh of points becomes too coarse for accurate evaluation of specific heats on account of the dominant effect of the low-frequency end of the spectrum. The sampling procedure gives too few frequencies in this region. The

computed values of C_v and Θ are, therefore, not reported for temperatures below 20°K .

IV. COMPARISON WITH EXPERIMENT

A. Alpha Iron

The neutron data obtained by Iyengar *et al.*⁴⁰ for this metal is confined to the $[100]$ direction and is less certain than the later work of Low.³⁸ Neither can much reliance be placed on Curien's³¹ diffuse x-ray scattering measurements on account of the experimental uncertainties inherent in the technique. We have, therefore, compared the results of our computations with the

⁴⁰ P. K. Iyengar, N. S. Satyamurthy, and B. A. Dassanacharya, in *Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, October, 1960* (International Atomic Energy Agency, Vienna, to be published).

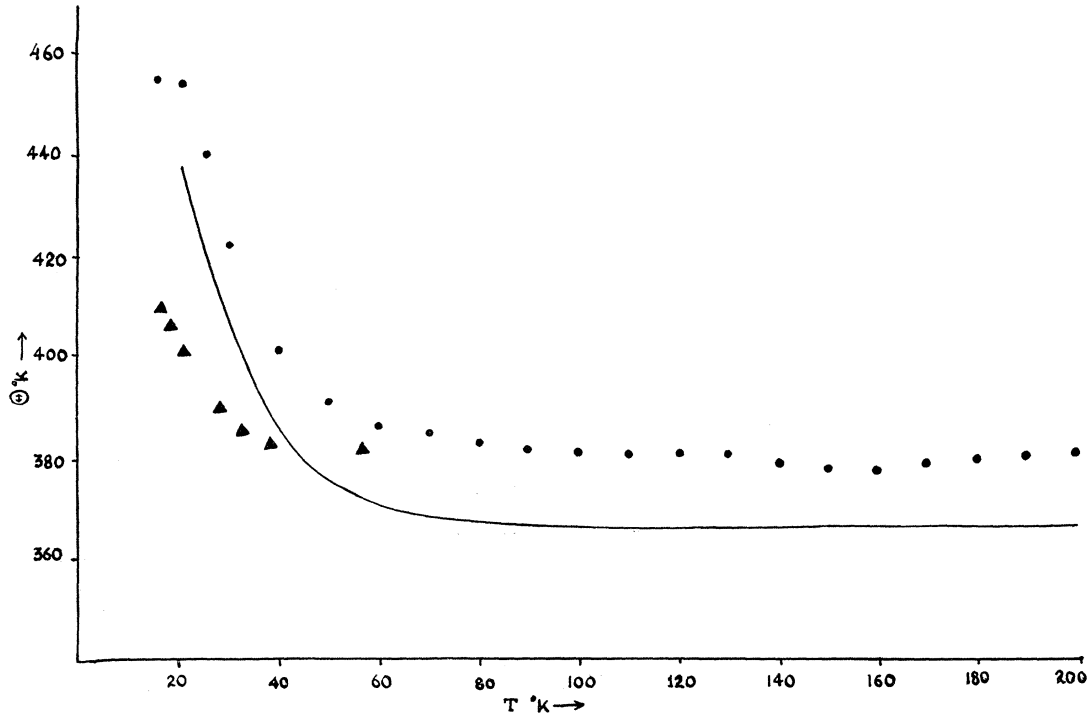


Fig. 8. Θ - T curve for molybdenum. Experimental data are ● Clusius and Franzosini (Ref. 50), ▲ Simon and Zeidler (Ref. 54).

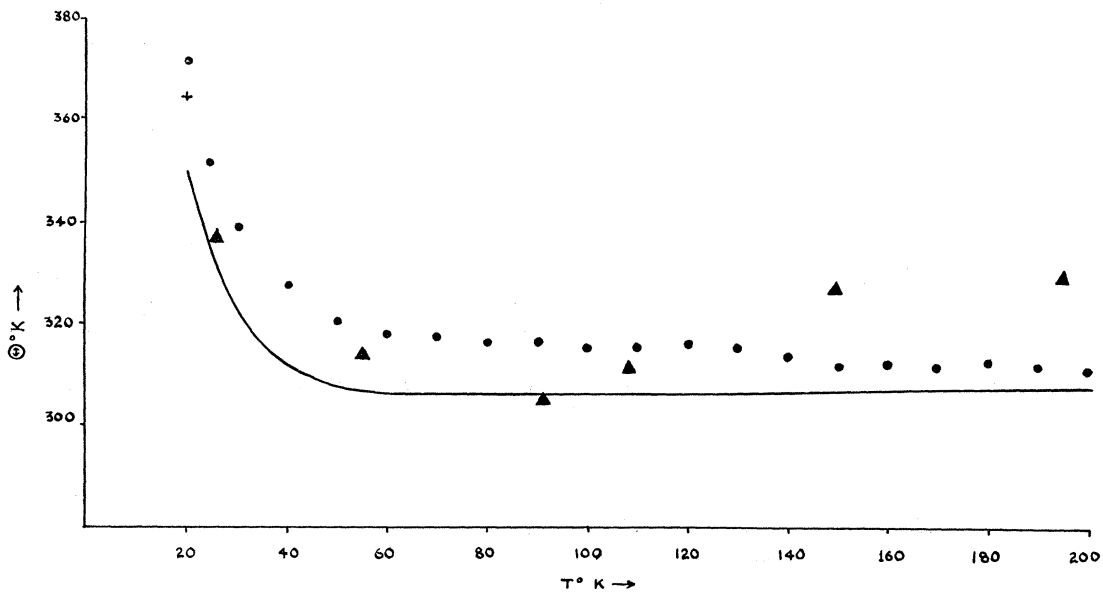


Fig. 9. Θ - T curve for tungsten. Experimental data are ● Clusius and Franzosini (Ref. 50), ▲ Lange (Ref. 55) and Zwicker (Ref. 56), + Walcott (Ref. 53).

measurements of Low. For the $[110]$ direction, however, Low has plotted one transverse branch only, and the data available for other branches are also scanty. Though there is fair agreement between the theoretical curves and the experimental frequencies (Fig. 1), still it is difficult to draw any definite conclusions, in view of insufficient data.

The experimental values of C_v have been taken from Duyckaerts⁴¹ and Kelley⁴² for temperatures below and above 50°K. In the absence of any recent data, the observations of Kelley have been preferred, as these are in broad agreement with those of Eucken and

⁴¹ G. Duyckaerts, *Physica* 6, 401 (1939).

⁴² K. K. Kelley, *J. Chem. Phys.* 11, 16 (1943).

TABLE III. Lattice specific heats in cal/mole-deg².

Element Temp. °K	α-Fe		Mo		W		
	Theoretical (a)	Ob- served (b)	Theo- retical	Ob- served	Theo- retical	Ob- served	
20	0.0442	0.0477	0.0140	0.0443	0.0398	0.0873	0.0724
30	0.1714	0.1800	0.1444	0.186	0.166	0.369	0.319
40	0.423	0.439	0.327	0.501	0.448	0.879	0.776
50	0.777	0.800	0.660	0.962	0.872	1.498	1.381
60	1.192	1.219	1.078	1.488	1.371	2.116	1.989
80	2.055	2.083	1.961	2.498	2.350	3.152	3.035
100	2.821	2.847	2.756	3.303	3.177	3.886	3.800
120	3.438	3.460	3.409	3.898	3.777	4.391	4.313
140	3.917	3.936	3.932	4.331	4.245	4.742	4.700
160	4.286	4.301	4.316	4.649	4.582	4.992	4.965
180	4.570	4.583	4.628	4.889	4.821	5.174	5.147
200	4.792	4.803	4.871	5.068	5.009	5.311	5.296

Werth⁴³ and Simon and Swain,⁴⁴ being on the average about 0.02 cal/mole higher than those of the former and less by the same amount than those of the latter except at about 150°K. Manning,¹⁴ from band-structure studies, has computed the value of the coefficient of the electronic specific heat to be 4.6×10^{-4} cal/mole deg². The experimental values of γ , 12.06 (Duyckaerts⁴¹), 12.06 ± 0.12 (Keesom and Kurrelmeyer⁴⁵), and 11.91 ± 0.22 (Cheng *et al.*⁴⁶) all of them in units of 10^{-4} cal/mole deg², are definitely much larger than the theoretical one. The reasons for this discrepancy are presently not understood. Rayne and Chandrashekar³⁵ have re-analyzed the data of Cheng *et al.* assuming the presence of a spin-wave contribution ($\alpha T^{3/2}$) to the heat capacity at low temperatures. They have used their low-temperature elastic data extrapolated to 0°K to evaluate the lattice contribution to the heat capacity, which is subtracted from the experimental value. The analysis of residual heat capacity yields the values $(11.7 \pm 0.1) \times 10^{-4}$ cal/mole deg² and $(2 \pm 1) \times 10^{-5}$ cal/mole deg^{5/2} for the coefficients of electronic and spin-wave contributions, respectively. The presence of the spin-wave contribution to the heat capacity for this metal has recently been confirmed experimentally by Tennenwald⁴⁷ (spin-wave resonance work) and Heatherly *et al.*⁴⁸ (small-angle neutron scattering). Dixon *et al.*⁴⁹ have calculated this contribution from the exchange-interaction term derived from neutron scattering data and have subtracted it from their calorimetric value. The residual part has been analyzed for the values of γ and α . Their values are $\gamma = (11.34 \pm 0.03) \times 10^{-4}$ cal/mole deg² and

⁴³ A. Eucken and H. Werth, Z. Anorg. Allgem. Chem. **188**, 152 (1930).

⁴⁴ F. Simon and R. C. Swain, Z. Physik. Chem. (Leipzig) **B28**, 189 (1935).

⁴⁵ W. H. Keesom and B. Kurrelmeyer, Physica **6**, 663 (1939).

⁴⁶ C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 2 (1960); **120**, 426 (1960).

⁴⁷ P. E. Tennenwald, *Proceedings of the International Conference on Magnetism and Crystallography* (The Physical Society of Japan, Bunkyo-Ku-Tokyo, 1962), p. 592.

⁴⁸ H. Heatherly, K. Hirikawa, R. D. Lowde, J. F. Mallett, M. W. Stringfellow, and B. H. Torrie, J. Appl. Phys. **35**, 802 (1964).

⁴⁹ M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. Roy. Soc. (London) **A285**, 561 (1965).

$\alpha = (1.15 \pm 0.09) \times 10^{-5}$ cal/mole deg^{5/2}. We have used the same values to evaluate the electronic and lattice-wave contributions, which have been subtracted from the experimental data to give the lattice specific heats (observed) in Table III.

The Θ - T curves (Fig. 7) exhibit a good agreement with experimental data in the middle region only. Towards the low-temperature end, the experimental values are consistently higher than the theoretical ones, while for temperatures above 120°K, there is a marked decrease in the value of the Debye parameter and the rate of decrease increases with the temperature.

B. Molybdenum

Woods and Chen² have given the dispersion curves for the symmetry directions for this metal and have also tabulated values for a few selected modes. There is general agreement between the theoretical curves and experimental data (Fig. 2), except near the zone boundaries in the [100] direction for the longitudinal branch and in the [110] direction for the transverse branches.

The experimental determination of C_v in the case of Mo has been made recently by Clusius and Franzosini.⁵⁰ Unlike the case of α -Fe, there is a good agreement between the theoretical and experimental values of electronic specific heat for this metal. Morin and Maita²³ have found a value of 4.8×10^{-4} cal/mole deg² for the superconducting phase, and have shown it to be consistent with the band structure of this metal. The other experimental values are 5.1 ± 0.4 (Horowitz and Daunt⁵¹), 5.25 ± 0.26 (Rayne⁵²) and 5.05×10^{-4} cal/mole deg² (Walcott⁵³). Clusius and Franzosini recommend a value of 5.0 ± 0.5 and 6.5 for temperatures up to and above 25°K. No valid theoretical reasons have been put forward for the latter value. We have, therefore, calculated the experimental values of lattice specific heats for Mo (Table III) from Clusius-Franzosini data with $\gamma = 5.0 \times 10^{-4}$ cal/mole deg² for the entire range of temperature, though a slightly lower value of γ would have improved the fit appreciably.

The general trend of the theoretical and experimental values (Fig. 8) is the same and the difference between them remains steady at about 3%. The Θ values for the earlier work of Simon and Zeidler⁵⁴ have also been shown in Fig. 8.

C. Tungsten

A careful study of the lattice dynamics of this metal, which has high thermal absorption and low coherent

⁵⁰ K. Clusius and P. Franzosini, Z. Naturforsch. **14a**, 99 (1959).

⁵¹ M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953).

⁵² F. Rayne, Phys. Rev. **95**, 1428 (1954).

⁵³ N. M. Walcott, in *Conference de Physique des Basses Températures, Paris, 1955* (Centre Nationale de la Recherche Scientifique and UNESCO, Paris, 1956), p. 206.

⁵⁴ F. Simon and W. Zeidler, Z. Physik. Chem. (Frankfurt) **123**, 387 (1962).

scattering cross section for neutrons, has been made by Chen and Brockhouse.¹ They have also reported the value of frequencies for a few modes. Figure 3 shows a very good agreement between theoretical curves and experimental data except that the two branches in [110] direction, though almost degenerate up to zone boundary, fail to cross each other as expected from experimental data.

Chen and Brockhouse have also calculated the frequency distribution function $G(\nu)$ using 23 force constants obtained from the 8th-neighbor best-fit curves for the experimental data. They report two pronounced peaks in the frequency distribution at 4.6 and 6.3×10^{12} sec^{-1} . The frequency distribution obtained by us (Fig. 6) also exhibits the two peaks at 4.6 and 6.4×10^{12} sec^{-1} .

Clusius and Franzosini⁵⁰ have also determined the specific heats in the case of tungsten. The earlier measurements for this metal were of Lange⁵⁵ and Zwikker⁵⁶ for the temperature ranges up to and above 91°K , respectively. The position regarding the electronic specific heat is not clear enough for W and there is considerable divergence in the values reported by different workers. Manning and Chodorow²⁴ have theoretically computed the γ value to be 4.8×10^{-4} cal/mole deg^2 . The experimental values, however, are 1.8 ± 0.7 (Horowitz and Daunt⁵¹), 3.5 ± 0.2 (Rayne⁵²), 2.89 (Walcott⁵³) and $2.65 \pm 0.24 \times 10^{-4}$ cal/mole deg^2 (Waite *et al.*⁵⁷). Clusius and Franzosini have recommended the values 2.7 and 4.9×10^{-4} cal/mole deg^2 for temperatures below and above 20°K . As in the case of Mo, we have evaluated lattice specific heats (Table III) from the data of Clusius and Franzosini with $\gamma = 2.7 \times 10^{-4}$ cal/mole deg^2 . In the Θ - T plot for this metal (Fig. 9), the values of Θ for other workers, referred to above, have also been shown. The agreement between the theoretical and experimental values of Θ is reasonably good.

⁵⁵ F. Lange, Z. Physik. Chem. (Leipzig) **110**, 343 (1924).

⁵⁶ C. Zwikker, Z. Physik **52**, 668 (1928).

⁵⁷ T. R. Waite, R. S. Craig, and W. E. Wallace, Phys. Rev. **104**, 5 (1956); **104**, 1240 (1956).

V. DISCUSSION AND CONCLUSION

In the present computations 300°K elastic-constant data were taken in order to have a check on our results with the room-temperature neutron-scattering data. The agreement between theoretical and experimental Θ values would have been within experimental errors ($\pm 1\%$) in the cases of Mo and W and appreciably improved for α -Fe if the low-temperature elastic constants were used. In the case of α -Fe, however, the difference between the experimental and theoretical values of C_v will persist even if the temperature dependence of the elastic constants is taken into consideration. This may be for several reasons: In the first place, the values of γ and α , which represent the contribution of the electrons and spin waves to the specific heats, are very uncertain. Secondly, it is also possible that the spin-wave contribution may not be exactly given by the term $\alpha T^{3/2}$ and α itself may be a function of temperature. In view of these uncertainties and the nonavailability of any reliable heat-capacity data, no clear picture emerges about this metal.

The special feature of Krebs's model in the present form is that, while using only three force constants, it provides agreement between the theoretical dispersion curves and the experimental data which is as good as that furnished by the curves computed by Low,²⁸ Woods and Chen,² and Chen and Brockhouse¹ with the help of seven force constants in the cases of α -Fe, Mo, and W, respectively.

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