

Anisotropic Dispersive Continuum Model for Lattice Dynamics of Solids

K. C. SHARMA AND S. K. JOSHI

Physics Department, Allahabad University, Allahabad, India

(Received 3 June 1963)

The frequency distribution functions of copper and lithium have been calculated by sampling method from 7770 points distributed in the Debye sphere, using the anisotropic dispersive continuum model. The specific heats are calculated by numerical integration. The calculated equivalent Debye temperatures are compared with the experimental data and the results are discussed.

I. INTRODUCTION

LATTICE vibrations play a dominant role in many physical phenomena. All those physical properties of a crystal which depend on the heat motion of the constituent particles require for their detailed explanation a knowledge of the actual form of the vibrational spectrum, about which very little is known. The complete spectrum of the lattice frequencies of a particular substance can not be described by a single simple function. Each case has to be worked out more or less laboriously. For a calculation of the properties of solids, it is convenient to have some simple lattice dynamical models, governed by a few parameters only, even at the cost of some loss of absolute accuracy. The Debye model, which has supreme simplicity, is normally used in such calculations. In this approximation the crystal anisotropy and the dispersion of the lattice waves are neglected. Fuchs¹ studies the effect of elastic anisotropy on the specific heat of lithium. Recently Collins² calculated the temperature variation of the coefficient of thermal expansion for materials of cubic structure using the anisotropic continuum model. The anisotropic continuum model does not give a good representation of the lattice spectrum. Its spectrum extends to higher frequencies than can occur in the discrete lattice and is smoothed out into a featureless band. At high temperatures the model overemphasizes the contribution from longitudinal modes.

The dispersion of the lattice waves causes the spectrum to be compressed towards smaller frequencies. In this paper the dispersion has been taken into account in a simple way. In order to be able to apply the model to various physical phenomena, it is imperative to test it by computing the specific heats of a few typical crystals and then compare them with experimental data. The vibrational spectra of lithium and copper are therefore examined using this model. The calculated Debye temperatures are compared with existing experimental results. The choice of the metals was dictated by the fact that the metals, copper and lithium, have been favorite subjects for theoretical and experimental studies of thermal properties.

II. THE DESCRIPTION OF THE MODEL

In the anisotropic dispersive continuum model, the anisotropic continuum model of Fuchs¹ is modified by inclusion of a dispersion factor. It is assumed that the dispersion is of the same form as given by the Born-von Kármán theory for a linear chain of equally spaced mass points, each point carrying the same mass and with interactions confined between nearest neighbors. The lattice frequencies $\omega_{q,i}$ are therefore given by

$$\omega_{q,i} = C_i(2Q/\pi)\sin(\pi q/2Q). \quad (1)$$

Here C_i are the velocities of sound waves with different polarizations given by the three roots of the third-order Christoffel equation³ for a particular direction of propagation vector \mathbf{q} . The Brillouin zone is replaced by a sphere (Debye sphere) of radius $Q = (6\pi^2N)^{1/3}$, where N is the number of unit cells per unit volume.

III. FREQUENCY SPECTRA AND SPECIFIC HEATS OF COPPER AND LITHIUM

The frequency spectra were calculated numerically using the sampling method.⁴ The reciprocal space was divided into a three-dimensional array of points. The frequencies were calculated at points of reciprocal space lying within irreducible trihedral angle. The sampling method can give an accurate spectrum only when the number of frequencies falling in a small frequency interval is fairly large. Since the number of frequencies per frequency interval in the low-frequency region is lowest, the error in the distribution itself is rather large. It is, therefore, very desirable to have a finer subdivision of q space in the central region, which will yield a reliable distribution of frequencies in the low-frequency region. In the higher-frequency region of the spectrum even a coarse mesh gives satisfactory results. In view of these facts we have adopted the following scheme of subdivision in reciprocal space. First a grid was obtained by dividing the Debye radii along the three axes in eight parts. Fineness of this mesh has been augmented by further subdivision by factors of 8 and 64 in regions of space enclosed between spheres of radii $\frac{1}{4}Q$ and $\frac{1}{2}Q$, $\frac{1}{8}Q$ and $\frac{1}{4}Q$, respectively. In the central regions inside the

¹ K. Fuchs, Proc. Roy. Soc. (London) **A157**, 444 (1936).

² J. G. Collins, Phil. Mag. **8**, 323 (1963).

³ A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, Inc., New York, 1944), p. 299.

⁴ M. Blackman, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII, Part I, p. 325.

sphere of radius $\frac{1}{3}Q$ the density of points was 512 times the density in the outermost region of the Debye sphere. This subdivision corresponds to a total of 7770 points distributed inside the sphere.

In order to calculate the frequency distribution function $G(\omega)$, the number of frequencies falling into intervals of 2.5×10^{12} rad/sec were counted. The statistical weights of $1/512$, $1/64$, $1/8$, and 1 were given to points lying in the four regions of different point densities inside the Debye sphere. In counting the points lying within the irreducible trihedral angle of q space, for which the frequencies alone were calculated, account was also taken of the fact of whether it lies on its faces or edges in the $[100]$, $[110]$, and $[111]$ directions. A histogram was drawn with step-width $\Delta\omega$. Five of these step curves were plotted, each shifted with respect to the previous one by 0.5×10^{12} rad/sec in the ω scale. A distribution curve is obtained out of these histograms by approximating them by a smooth curve.

The smoothed frequency distributions for copper and lithium are shown in Figs. 1 and 2. The curves have not been normalized and the units of $G(\omega)$ are arbitrary. The elastic constants used in this calculation refer to a

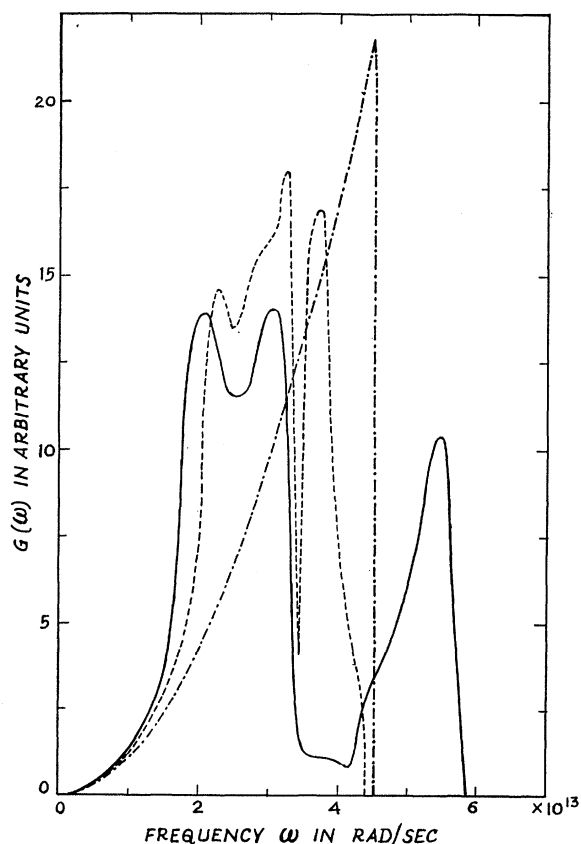


FIG. 1. The lattice vibrational spectrum of copper. The smooth solid curve is obtained in the present calculation. The dashed curve gives the spectrum obtained by Jacobsen; the Debye spectrum is represented by the dash-dotted curve.

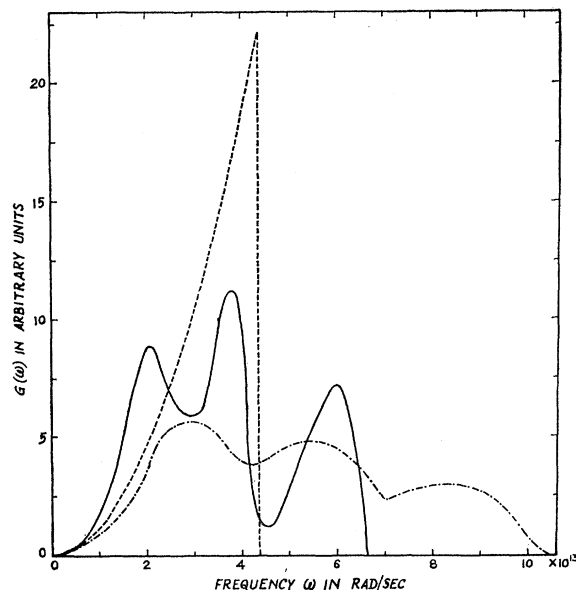


FIG. 2. The frequency spectrum of lithium. Solid line, the spectrum calculated using anisotropic dispersive continuum model. Dash-dot line, the spectrum calculated by Fuchs using anisotropic continuum model. Dashed line, the Debye spectrum for lithium.

temperature of 0°K . The values of these and the other constants needed in the calculation are given in Table I. For copper the elastic constants at 0°K given in the table are extrapolated from the measurements performed at 4.2°K by Overton and Gaffney.⁵ In the case of lithium these are extrapolated from the values given by Nash and Smith⁶ near 77°K .

The specific heat is given by the usual expression:

$$C_v = k \int_0^{\omega_{\max}} \frac{G(\omega) (\hbar\omega/kT) e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} d\omega, \quad (2)$$

where all the symbols have their usual significance. From the distribution curve, the specific heat was obtained by graphical integration. The comparison with experimental data on specific heats is made as is customary, in terms of equivalent Debye temperature (the value of Θ at a given temperature which will correctly reproduce the lattice heat capacity at that temperature when used in Debye theory). The equivalent Θ - T curves for copper and lithium are plotted in Figs. 3 and 4.

IV. DISCUSSION

For convenience it is better to separate the discussion for copper and lithium.

⁵ W. C. Overton and J. Gaffney, Phys. Rev. **98**, 969 (1955).

⁶ H. C. Nash and C. S. Smith, J. Phys. Chem. Solids **9**, 113 (1959).

A. Copper

The experimental data for the specific heat have been taken from Franck, Manchester, and Martin⁷ between 0.4 and 30°K, from Martin⁸ between 20 and 30°K, and from Giauque and Meads⁹ between 10 and 300°K. The experimental specific heats at lower temperatures are corrected for the electronic contribution. The C_v measurements by different workers are quite consistent. A particularly striking fact in Fig. 3 is the appearance of about the right depth and position of the minimum. The calculated curve lies slightly low in the low-temperature region. This suggests that the values of ω by (1) are lower than the actual values in the low-frequency region, i.e., the model overestimates the dispersion for lower frequencies, hence, overestimates the specific heat and underestimates the values of Θ . In the same way it can be argued from the disagreement at the high-temperature region that the dispersion is underestimated at high frequencies. These assumptions were verified by comparing the calculated dispersion curves on this model with the curves due to Cribier *et al.*¹⁰ from their experiments on slow neutron scattering and with curves of Jacobsen¹¹ deduced from the measurement of the intensity of diffuse scattering of x rays from a copper single crystal. The difference between the observed and calculated Θ never exceeds 6%.

At the extreme low-frequency end of the spectrum sampling was performed at frequency intervals $\Delta\omega = 1 \times 10^{12}$ rad/sec. It was found that the ω^2 law was

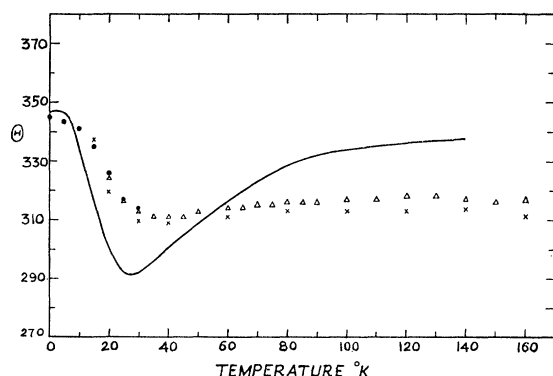


FIG. 3. Equivalent Debye Θ versus temperature for copper. The solid curve is the theoretical one obtained from the frequency spectrum shown in Fig. 1. Solid circles represent the experimental values of Franck *et al.* Triangles are taken from the measurement of Martin. Crosses denote the measured values due to Giauque and Meads.

⁷ J. P. Franck, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).

⁸ D. L. Martin, Can. J. Phys. **38**, 17 (1960).

⁹ W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941).

¹⁰ D. Cribier, B. Jacrot, and D. Saint-James, J. Phys. Radium **21**, 67 (1960); *International Atomic Energy Agency Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, October, 1960* (International Atomic Energy Agency, 1961), p. 549.

¹¹ E. H. Jacobsen, Phys. Rev. **97**, 654 (1955).

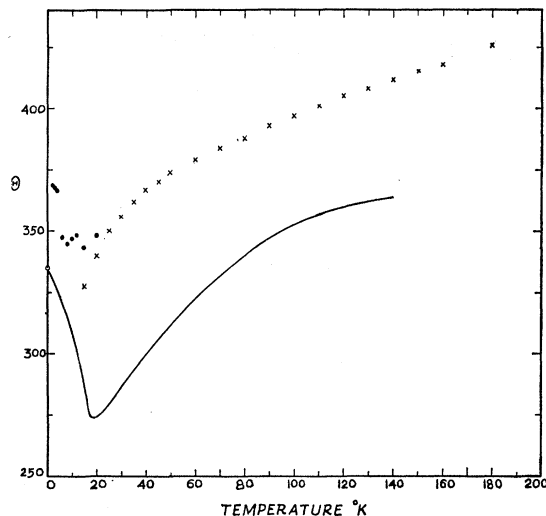


FIG. 4. Equivalent Debye characteristic temperature as a function of temperature for lithium. Solid curve is calculated from the frequency spectrum shown in Fig. 2. The solid circles correspond to the experimental data of Roberts, and crosses represent the experimental measurements of Simon and Swain.

valid for very low frequencies. Therefore, as is expected, as the temperature of the solid approaches 0°K the present model gives results identical to those from simple Debye model. The extrapolated value of $\Theta(0)$ calculated by us is in excellent agreement with the accurately known calorimetric $\Theta(0)$ value of Franck *et al.*,⁷ Corak *et al.*,¹² and Rayne¹³ and also with the Θ (elastic) calculated directly¹⁴ from the elastic constants at 0°K by averaging the inverse cube of elastic wave velocities over all directions of propagation.

Jacobsen calculated a frequency spectrum of copper from a force-constant model fitted to his experimental frequency wave-number relations obtained from the diffuse x-ray scattering measurement. Jacobsen's spectrum corresponds to room-temperature data, and is obtained from a sampling of 3417 points distributed uniformly in 1/48 of the Brillouin zone. In Fig. 1 we have plotted his spectrum also, which agrees in its broad features with the spectrum calculated by us.

B. Lithium

Many of the comments made in the case of copper are relevant here too. There are a few more points. The disagreement between the experimental and theoretical Θ - T curves is more pronounced. It is seen that the theoretical and the experimental Θ - T curves are similar but the theoretical values are uniformly lower than the experimental values by about 14%. The experimental values of C_v in the range 15 to 300°K are due to Simon

¹² W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **98**, 1699 (1955).

¹³ J. Rayne, Australian J. Phys. **9**, 189 (1956).

¹⁴ G. A. Alers and J. R. Neighbours, Rev. Mod. Phys. **31**, 675 (1959).

TABLE I. Constants of copper and lithium extrapolated to 0°K. The elastic constants are in units of 10^{12} dynes/cm². Ω is the atomic volume and ρ the density at 0°K.

	C_{11}	C_{12}	C_{44}	ρ (g cm ⁻³)	Ω^{-1} (10 ²² cm ⁻³)
Copper	1.762	1.2494	0.8177	9.018	8.553
Lithium	0.1574	0.1333	0.1158	0.5471	4.748

and Swain,¹⁵ while those in the range 2 to 20°K are due to Roberts.¹⁶ Experimental $\Theta(0)$ shown at 0°K was determined by Martin¹⁷ from the slope of a plot of C_p/T versus T^2 from his measurements of the specific heat of natural lithium between 0.4 and 1.5°K. The calorimetric data are quite scattered and Martin has pointed out that the interpretation of the experimental results of Roberts is not very certain because of the use of helium exchange gas within the calorimeter. Unfortunately, the situation is further complicated by the fact that lithium undergoes a martensitic (or diffusionless) transformation on cooling below about 80°K, when some of the body-centered cubic phase transforms

to a faulted close-packed phase.^{18,19} The fact that the two different phases will have different specific heats is guaranteed by thermodynamic requirements. Because of the occurrence of the transformation we can not make a rigorous comparison of our calculation based on a cubic structure of lithium, with the experimental data of uncertain accuracy.

We have neglected the effects of anharmonicity. Comparison of the experimental $\Theta(T)$ and specific heat with the results of the calculation should be made in the temperature region corresponding to the choice of the parameters used in the calculation. The results of the entire work of the present calculation are estimated to be correct within 1%. All the calculations were performed with the help of a Remington Rand desk calculator.

From the present study it emerges that the anisotropic dispersive continuum model gives a reasonable, though by no means detailed, agreement with experiments. It is felt, therefore, that the use of this model in a calculation of a physical property of a crystal in place of usual Debye approximation will be more realistic. It is pertinent to point out again that more accurate but more complicated models would burden such a calculation too much.

¹⁵ F. Simon and R. C. Swain, *Z. Physik Chem.* **B28**, 189 (1935).

¹⁶ L. M. Roberts, *Proc. Phys. Soc. (London)* **B70**, 744 (1957).

¹⁷ D. L. Martin, *Proc. Roy. Soc. (London)* **A263**, 378 (1961).

¹⁸ C. S. Barret, *Acta Cryst.* **9**, 671 (1956).

¹⁹ D. L. Martin, *Proc. Roy. Soc. (London)* **A254**, 444 (1960).