

Anisotropic Dispersive Continuum Model for Lattice Dynamics of Solids. II

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The temperature variation of the Debye-Waller factor is calculated for copper on the basis of the anisotropic dispersive continuum model. The results are compared with x-ray measurements of Flinn *et al.* and the other theoretical calculations of this factor from different Born-von Kármán force models. The Debye-Waller factor is not very sensitive to the details of the frequency spectrum. The frequency distribution function for vanadium is also calculated on the basis of the anisotropic dispersive continuum model. The results of this calculation, as well as many other force-model calculations, yield a poor representation of the frequency spectrum, for which experimental measurements from the inelastic incoherent neutron scattering techniques are available.

I. INTRODUCTION

RECENTLY it was shown¹ that the anisotropic dispersive-continuum model gives a reasonable description of the lattice dynamics of solids and is convenient enough for a calculation of a physical property governed by the details of the phonon spectrum. This model provides a satisfactory explanation of the temperature variation of the Grüneisen parameter for copper.² It was thought worthwhile to compute the Debye-Waller factor on the basis of this model and to compare it with the values predicted for it from various other models and also with experimental results in the case of copper. We have also presented a calculation of the frequency spectrum of vanadium on the basis of this model and have compared it with an experimentally determined frequency spectrum.

II. DEBYE-WALLER FACTOR

The Debye-Waller factor enters into a large number of solid-state phenomena such as the Mössbauer effect, neutron scattering, x-ray diffraction, electrical conductivity, etc., and can also be correlated with the thermodynamic data, like specific heat. Recently, Flinn *et al.*³ reported on the x-ray determination of the Debye-Waller factor for copper by making x-ray intensity measurements from 4–500°K. They were able to interpret the experimental results in terms of a central-force model with first- and second-neighbor interactions. DeWames *et al.*⁴ have discussed the Debye-Waller factor of copper predicted by various force-constant models in the face of the experiments of Flinn *et al.* It would be interesting to compare the Debye-Waller factor calculated on the basis of the simple anisotropic dispersive continuum model with the earlier experimental and theoretical findings.

A. Theory

In the expression giving the intensities of the non-resonant elastically scattered waves (of slow neutrons,

¹ K. C. Sharma and S. K. Joshi, *Phys. Rev.* **132**, 559 (1963).

² K. C. Sharma and S. K. Joshi, *Phil. Mag.* **9**, 507 (1964).

³ P. A. Flinn, G. M. McManus, and J. A. Rayne, *Phys. Rev.* **123**, 809 (1961).

⁴ R. E. DeWames, T. Wolfram, and G. W. Lehman, *Phys. Rev.* **131**, 528 (1963).

x rays, etc.), from scatterers which are bound in crystals, the effect of the zero point and temperature motion of the scatterer is contained in the Debye-Waller factor which multiplies the fixed scatterer intensities, and is given by

$$f = e^{-2W},$$

where

$$2W = \frac{\hbar}{mN} \sum_{q,j} \frac{\{(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{e}_{qj}\} (n_{qj} + \frac{1}{2})}{\omega_{qj}}. \quad (1)$$

For a monatomic lattice of cubic symmetry, the exponent $2W$ is completely determined by the lattice vibrational frequency spectrum and is proportional to

$$X(T) = \frac{1}{3N} \sum_{q,j} \frac{1}{\hbar \omega_{qj}} \frac{\hbar \omega_{qj}}{2kT}. \quad (2)$$

In these expressions N is the total number of unit cells in the crystal, \mathbf{s} and \mathbf{s}_0 the wave vectors of the scattered and incident waves, \mathbf{e}_{qj} the polarization vector of the vibrational wave with frequency ω_{qj} and average population n_{qj} , k the Boltzmann constant, T the absolute temperature, \hbar the Planck's constant divided by 2π , and the summation is over all the wave vectors q and polarization branches j . Replacing the summation over q by an integration, Eq. (2) reduces to

$$X(T) = \frac{1}{3N} \frac{V}{8\pi^3} \sum_j \int \int \frac{q^2}{\hbar \omega_{qj}} \coth \frac{\hbar \omega_{qj}}{2kT} d\omega d\Omega. \quad (3)$$

Here Ω is the solid angle in wave-vector space. In the anisotropic dispersive continuum model the frequency wave vector relation is of the form

$$\omega_{qj} = C_j (2Q/\pi) \sin(\pi q/2Q), \quad (4)$$

where C_j are the velocities of sound with different polarizations, given by the three roots of the third-order Christoffel equation and the Brillouin zone is replaced by a Debye sphere of radius Q . Therefore,

$$X(T) = \frac{1}{3N} \frac{V}{8\pi^3} \sum_j \left(\frac{2Q}{\pi} \right)^3 \times \int_0^{\omega_{\max}} \int_0^{4\pi} \frac{1}{\hbar \omega} \frac{(\sin^{-1} \omega/a)^2}{(a^2 - \omega^2)^{1/2}} \coth \frac{\hbar \omega}{2kT} d\omega d\Omega. \quad (5)$$

TABLE I. The values of $X(T)$ for copper (in $eV^{-1}\times 10^6$).

Temperature (°K)	Θ (°K)	Experimental $X(T)$	Anisotropic dispersive continuum model		$X_D(T)$ (Debye approximation with $\Theta=335^\circ\text{K}$)
			$X(T)$ (Debye-Waller frequency integral)	$X(T)$ (Houston's method)	
30	317.7±10	0.547±0.017	0.626	0.551	0.520
50	317.7±10	0.638±0.026	0.684	0.597	0.595
100	319 ±10	0.861±0.042	0.955	0.844	0.796
200	330 ±10	1.373±0.078	1.658	1.479	1.335
300	315 ±10	2.170±0.135	2.387	2.239	1.922
400	300 ±10	3.127±0.209	3.173	3.080	2.523
500	307 ±10	3.733±0.240	4.019	3.973	3.141

Here $a=2C_jQ/\pi$. $X(T)$ can also be written directly from (3) in terms of the frequency-distribution function $G(\omega)$:

$$X(T) = \frac{1}{3N} \int_0^{\omega_{\max}} \frac{1}{\hbar\omega} \frac{\hbar\omega}{2kT} G(\omega) d\omega, \quad (6)$$

hereafter called the "Debye-Waller frequency integral."

B. Results and Discussion

$X(T)$ was evaluated from (5) and (6) separately. In the evaluation of $X(T)$ from (5), the integration over ω was performed numerically and the integration over Ω was carried out by using a modified Houston's spherical six-term integration procedure as developed by Betts *et al.*⁵ The six directions used in this procedure are [001], [101], [111], [102], [112], and [212]. In this particular method we have taken account of anharmonicities in an approximate way by considering the temperature variation of the elastic constants and the thermal expansion of the lattice in the computation of lattice frequencies. The pertinent elastic data at different temperatures are due to Overton and Gaffney⁶ and the lattice parameter values at various temperatures are from Pearson.⁷ To compute $X(T)$ from the Debye-Waller frequency integral (6), use was made of the frequency distribution function for copper corresponding to 0°K calculated in an earlier paper,¹ and the integration was performed numerically.

The values of $X(T)$ calculated in the above-mentioned two ways have been given at different temperatures in Table I along with the experimental data. The frequency distribution function $G(\omega)$, calculated by sampling method can not be very accurate at the extreme low-frequency end because of the coarseness of the mesh used. It is therefore thought that at low temperatures where lower frequencies have a predominating influence, Houston's method will yield more

reliable values of $X(T)$. This is evident from the better agreement with the experimental results of $X(T)$ values deduced from Houston's method in comparison to those obtained from the Debye-Waller frequency integral. On the other hand, Houston's method becomes unreliable at high frequencies. Therefore the high-temperature $X(T)$ values given by this method will not be accurate. But at high temperatures (say greater than 300°K) anharmonicities will have a slightly vitiating influence on our findings.^{7,8} As pointed out above we have considered anharmonicity when using Houston's procedure. For the sake of comparison we have also given $X(T)$ values calculated on the basis of the Debye model using $\Theta=335^\circ\text{K}$. The defining equation for $X(T)$ in the Debye approximation is

$$X_D(T) = \frac{9N\hbar^2}{kT} \left[\frac{1}{4x} + \frac{1}{x^3} \int_0^x \frac{y}{e^y - 1} dy \right],$$

with $x=\Theta/T$. Our results indicate that the Debye model does not yield satisfactory results. If we compare the values of $X(T)$ deduced by DeWames *et al.*⁴ from various other Born-von Kármán force models, we find that the Debye-Waller factor is quite insensitive to the details of the frequency spectrum and can yield little detailed information about the actual frequency spectrum.

III. FREQUENCY SPECTRUM OF VANADIUM

Eisenhauer *et al.*¹⁰ and Stewart and Brockhouse¹¹ have used the inelastic incoherent neutron-scattering technique to measure the lattice vibration spectrum of vanadium. Recently the frequency spectrum has again been measured experimentally at 206, 300, and 806°K by Turberfield and Egelstaff.¹² The neutron-scattering cross section of vanadium is almost entirely incoherent

⁸ A. A. Maradudin and P. A. Flinn, *Phys. Rev.* **129**, 2529 (1963).

⁹ H. Hahn and W. Ludwig, *Z. Physik* **161**, 404 (1961).

¹⁰ C. M. Eisenhauer, I. Pelah, D. J. Hughes, and H. Palevsky, *Phys. Rev.* **109**, 1046 (1958).

¹¹ A. T. Stewart and B. N. Brockhouse, *Rev. Mod. Phys.* **30**, 250 (1958).

¹² K. C. Turberfield and P. A. Egelstaff, *Phys. Rev.* **127**, 1017 (1962).

⁵ D. D. Betts, A. B. Bhatia, and M. Wyman, *Phys. Rev.* **104**, 37, (1956).

⁶ W. C. Overton and J. Gaffney, *Phys. Rev.* **98**, 969 (1955).

⁷ W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, (Pergamon Press, Inc., New York, 1958), p. 570.

and the frequency-distribution function $G(\omega)$ can be obtained directly from the measured energy distribution of the neutrons scattered from a polycrystalline sample of the material. Vanadium is one of the most anisotropic cubic (body-centered) crystals, and the various Born-von Kármán force-constant models yield a very poor representation of the frequency distribution of vanadium.¹³⁻¹⁶ It would be interesting to see how the anisotropic dispersive continuum model works on vanadium.

The procedure for calculating the frequency spectrum based on the anisotropic dispersive continuum model is exactly the same as has been already described in detail in an earlier paper.¹ Figure 1 shows the smoothed calculated frequency distribution curve together with the experimental curve of Eisenhauer *et al.*¹⁰ For comparison we have also shown the curves calculated by Hendricks *et al.*¹⁴ for a noncentral three-force-constant model and by Clark *et al.*,¹⁶ for a noncentral four-constant model. The curves have been normalized to the same area. Because of the uncertainty in the upper end of the experimental curve, we have arbitrarily cut it off at 5.65×10^{13} rad/sec for normalization. The room-temperature elastic constants for vanadium are those of Alers¹⁷ and are given below together with other pertinent data:

$$C_{11} = 22.795 \times 10^{11} \text{ dyn-cm}^{-2},$$

$$C_{12} = 11.870 \times 10^{11} \text{ dyn-cm}^{-2},$$

$$C_{44} = 4.255 \times 10^{11} \text{ dyn-cm}^{-2},$$

$$\text{density, } \rho = 6.022 \text{ gm-cm}^{-3},$$

$$\text{atomic volume, } \Omega = 13.879 \text{ \AA}^3.$$

Several features of the frequency distribution curves are of interest. The calculated and experimental frequency distributions are quite different with regard to the location of the two peaks, with the calculated frequency distributions having more widely spread maxima. In addition the high-frequency peak of the experimental curve is more intense than the low-frequency one, whereas all the calculations lead to just the opposite result. The maximum frequency of our calculated spectrum is in fair agreement with experiment, although the experimental value is not very well defined. Our calculation is somewhat nearer in results

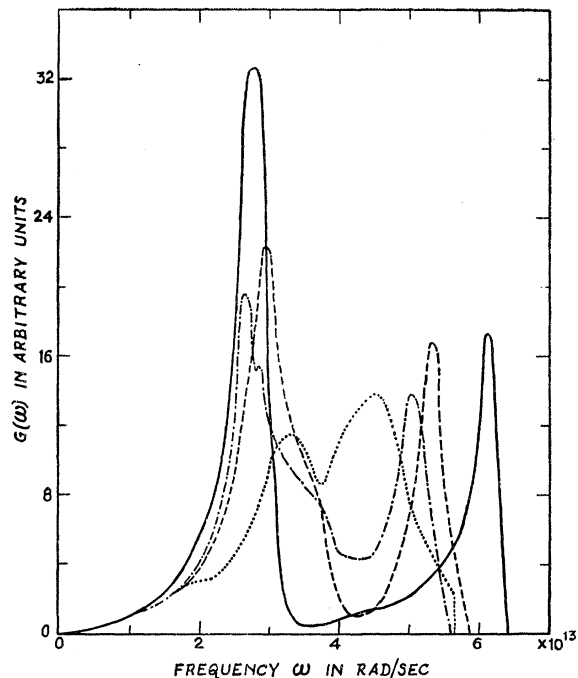


FIG. 1. The frequency spectrum of vanadium. The smooth solid curve is the spectrum calculated using the anisotropic dispersive continuum model; the dashed curve is the spectrum calculated by Hendricks *et al.* using a noncentral three-force-constant model; the dash-dot curve is calculated from the four-constant model of Clark *et al.*; and the dotted curve is obtained from the neutron scattering experiments of Eisenhauer *et al.*

to calculations based on de Launay's three-constant model than that from the four-constant model of Clark, Gazis, and Wallis. It appears that vanadium has something special about its lattice dynamics. The interesting experiments of Turberfield and Egelstaff¹² show a tail of the frequency spectrum at high frequencies, and also that the spectrum does not obey the Debye ω^2 law at the lowest frequencies at which they were able to make measurements. No explanation of these effects has been given at the present time. An experimental investigation of the dispersion curves for the lattice waves through diffuse x-ray scattering would be revealing and would throw much light on the lattice dynamics of vanadium.

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¹³ C. B. Clark, *J. Grad. Res. Center* **29**, 10 (1961).

¹⁴ J. B. Hendricks, H. B. Riser, and C. B. Clark, *Phys. Rev.* **130**, 1377 (1963).

¹⁵ B. Sharan, *J. Chem. Phys.* **36**, 1117 (1962).

¹⁶ B. C. Clark (private communication). We are indebted to G. A. Alers for bringing the work of Clark, Gazis, and Wallis to our notice.

¹⁷ G. A. Alers, *Phys. Rev.* **119**, 1532 (1960).