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Lattice Vibrations and Debye Temperatures of Aluminum

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The vibrational spectrum of a solid having nearest-neighbor central and noncentral force interactions was calculated for the case of aluminum. For this model the specific heat and Debye-Waller factor were obtained and found to be in good agreement with experimental values.

INTRODUCTION

IN an earlier paper,[1] referred to herein as I, the Debye-Waller factor and the specific heat of copper were calculated from the frequency spectrum of a solid having first- and second-neighbor central force interactions, and found to give close agreement with experimental values. A similar procedure has now been applied to aluminum. For this we measured the Debye-Waller factor of aluminum over the temperature range 4.2 to 400°K and calculated the frequency spectrum using as a model a solid with nearest-neighbor central and noncentral force interactions.

DETAILS AND RESULTS

X-ray measurements were made on a flat single crystal of aluminum, with faces cut parallel to the (100) planes. This was polished electrolytically and annealed in vacuum. The crystal was mounted in the x-ray cryostat described in I, and integrated intensity measurements were made using crystal monochromated Ag $K\beta$ radiation. At 4.2 and 77°K we measured the (600), (800), (1000), (1200), (1400), and (1600) reflections; while at 200, 300, and 400°K only the (600), (800), (1000), and (1200) reflections were used. The intensities were determined by the method given in a previous paper,[2] and the temperatures were obtained in the same manner as in I.

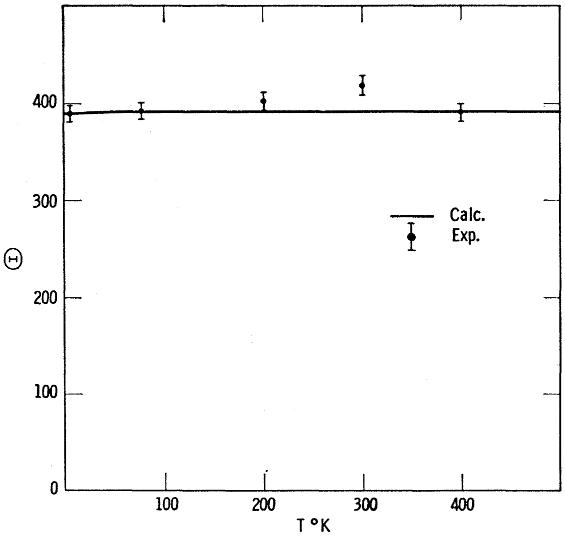

FIG. 1. The calculated and experimental effective x-ray Θ's.

For a Debye model of a solid, the Debye-Waller factor is

$$2M=\frac{12h^2}{mk\Theta}\left\{\frac{\phi(X)}{X}+\frac{1}{4}\right\}\left(\frac{\sin\theta}{\lambda}\right)^2,$$

where Θ is the Debye temperature and $X=\Theta/T$. The other constants have their usual meaning, and $\phi(X)$ is the function

$$\phi(X)=\frac{1}{X}\int_0^X\frac{ZdZ}{e^Z-1}.$$

If we regard the Debye approximation to apply at all temperatures, the effective Θ measured experimentally is, therefore, temperature dependent and can be compared directly with the Θ obtained by the calculation of $2M$ from the frequency spectrum. As in I, the observed x-ray intensity can be written as

$$\ln I=\ln J-(A\sigma^2/\Theta)\{[\phi(X)/X]+\tfrac{1}{4}\},$$

where J is the initial incident intensity and A is a constant. Taking differences between the intensity values at low and at high temperatures as in I, the high temperature Θ's can be determined. Since this method is not suitable for low temperatures, an iterative scheme was adopted: assuming a value for Θ_0, the $\ln J$'s can be determined, and from these values of Θ_{77}, Θ_{200}, etc., are

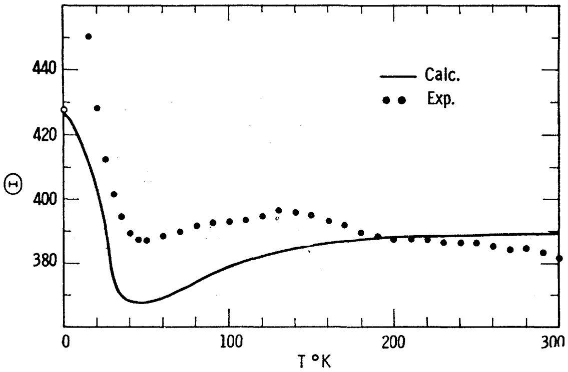

FIG. 2. Calculated and experimental effective calorimetric Θ's. The value at 0°K (open circle) is due to Phillips (Ref. 4).

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

[2] P. A. Flinn, G. M. McManus, and J. A. Rayne, J. Phys. Chem. Solids **15**, 189 (1960).

obtained. When the high temperature Θ's agree with those previously obtained, the proper values of Θ_0 and Θ_{77} are determined. These x-ray Θ's are shown in Fig. 1. The corresponding specific heat Θ's, taken from the work of Giauque and Meads,[3] and corrected for the electronic contribution,[4] are shown in Fig. 2.

The specific heat and the Debye-Waller factor are given in terms of the eigenvalues ω_{ij} of the dynamical matrix by the expressions[5]

$$C_v=k\sum_{ij}\xi_{ij}{}^2e^{\xi_{ij}}/(e^{\xi_{ij}}-1)^2$$

$$2M=\frac{16}{3}\frac{\pi^2\hbar}{mN}\left(\frac{\sin\theta}{\lambda}\right)^2\sum_{ij}\frac{1}{\omega_{ij}}\left\{\frac{1}{2}+\frac{1}{e^{\xi_{ij}}-1}\right\},$$

where $\xi_{ij}=\hbar\omega_{ij}/kT$. As a model, we chose a solid having only nearest-neighbor central and noncentral force interactions. This was chosen rather than the central force model used in I because the Cauchy relation is even more poorly satisfied for aluminum than for copper. The present model makes full use of the three elastic constants, rather than just two in the central force model, and so does not necessitate the Cauchy relation. The secular determinant for this case is just that used by Walker,[6] but with second- and third-neighbor interactions missing; such a model has already been investigated for other structures.[7] For this model, the elements of the dynamical matrix are

$$d_{ii}=\frac{4}{\rho a^2}\{(c_{11}+2c_{44})-c_{11}C_i(C_j+C_k)+(c_{11}-2c_{44})C_jC_k\},$$

$$d_{ij}=\frac{4}{\rho a^2}(c_{12}+c_{44})S_iS_j,$$

where $C_i=\cos\pi aK_i$, $S_i=\sin\pi aK_i$, a is the lattice parameter, and ρ is the density. The elastic moduli used were those obtained at 4.2°K by Kamm and Bohm[8]:

$$c_{11}=1.143\times10^{12}\ \text{dyn/cm}^2,$$

$$c_{12}=0.6204\times10^{12}\ \text{dyn/cm}^2,$$

$$c_{44}=0.3171\times10^{12}\ \text{dyn/cm}^2.$$

The dynamical matrix was diagonalized by the usual Jacobi reduction scheme at 5600 points in $\frac{1}{16}$th of the full zone in **K** space. The frequency spectrum for this model is shown in Fig. 3. Using these eigenvalues, C_v and $2M$ were evaluated at 20° intervals between 20 and 400°K. At 0°K, the specific heat Θ obtained from deLaunay's formula[9] is $\Theta_0=426$°K, in good agreement with the calorimetric value of $\Theta_0=427.7$°K found by Phillips.[4] The x-ray Θ at 0°K is given by the first inverse moment of the frequency spectrum

$$\Theta_{xr}(\mathrm{o})=\frac{3}{2}\frac{\hbar}{k}\frac{1}{\mu_{-1}},\quad \mu_{-1}=\frac{1}{3N}\sum_{ij}\frac{1}{\omega_{ij}},$$

and this yields $\Theta_{xr}(\mathrm{o})=390$°K. We also calculated C_v and 2_M on the basis of a solid with first- and second-neighbor central force interactions; this gave specific heat Θ's about 40° lower than that shown in Fig. 2, and x-ray Θ's about the same as in Fig. 1, except for much lower values at low temperatures.

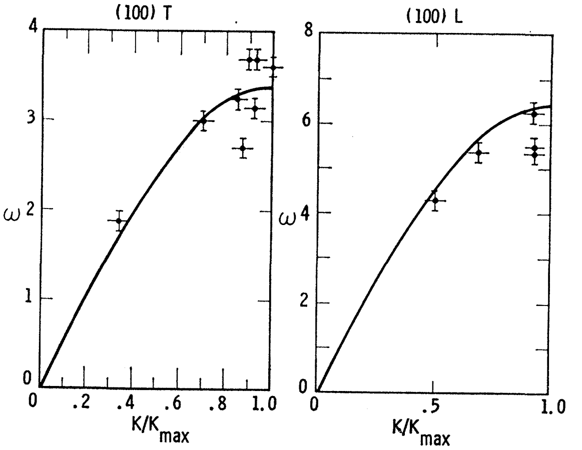

FIG. 4. Dispersion curves for longitudinal (L) and transverse (T) modes in the [100] direction. The experimental points are from Brockhouse (Ref. 13). ω is in units of 10^{13} sec^{-1}.

DISCUSSION

The agreement between calculation and experiments is seen to be very good for the x-ray Θ's (the precise

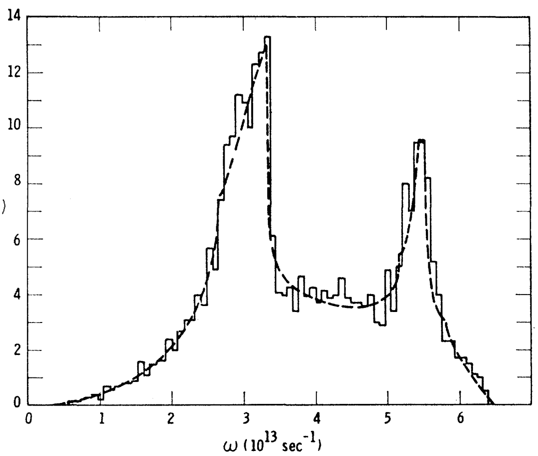

FIG. 3. The frequency spectrum histogram of aluminum. The dashed curve is the probable shape, based on the critical points.

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

[4] N. E. Phillips, Phys. Rev. **114**, 676 (1959).

[5] This corrects an error in transcription appearing in Eqs. (7) and (8) of I.

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[7] B. C. Clark, M.S. thesis, Kansas State University, 1963 (unpublished).

[8] G. N. Kamm and H. V. Bohm, Phys. Rev. **131**, 111 (1963).

[9] J. deLaunay, J. Chem. Phys. **22**, 1676 (1954).

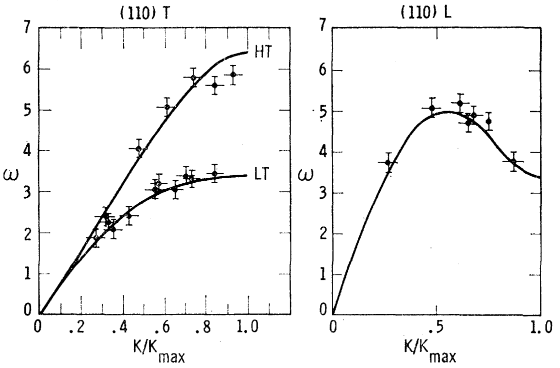

FIG. 5. Dispersion curves for the [110] direction. The experimental points are from Brockhouse (Ref. 13).

agreement at low temperatures is probably fortuitous), but only fair for the specific heat Θ's. However, in the case of the specific heat Θ's the agreement is difficult to assess, since the recent determination of the heat capacity near 0°K by Phillips[4] clearly indicates that the low-temperature calorimetric values of Giauque[3] are incorrect. If the values at higher temperatures are correct, then the agreement between experiment and calculation is quite good. As it stands, this simple model agrees more closely with experiment than does Walker's[6] nine-constant model, corrected for anharmonicities. It is worth remarking that Flinn and Maradudin[10] have evaluated the contribution of the cubic and quartic anharmonic terms to the specific heat of a solid having nearest-neighbor central force interactions. Their expressions, in the case of aluminum, gives an anharmonic correction of less than $2\frac{1}{2}\%$ in the low-temperature limit.

The frequency spectrum shown in Fig. 3 differs considerably from Walker's[6] spectrum, but less so from that obtained by Squires.[11] For the secular equation used in this paper, the analytic critical points in the frequency spectrum can be located at symmetry points and along symmetry axes of the Brillouin zone,[12] although there may be generalized critical points inside the zone that are not included in the symmetry set. These extra critical points were found from the contours of constant frequency in the zone, and the shape of the spectrum from the complete set of critical points is given in Fig. 3.

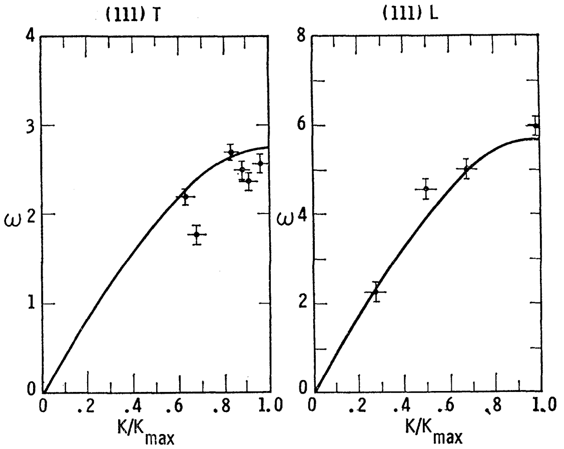

FIG. 6. Dispersion curves for the [111] direction. The experimental points are from Brockhouse (Ref. 13). In these three figures, the error estimates on the experimental points are not as accurately reproduced as are the points themselves.

Using the constant frequency contours, the dispersion curves in the principal directions were determined and are shown in Figs. 4–6. The experimental values shown with these curves are those obtained by Brockhouse[13] from neutron inelastic scattering. For this simple model the agreement is surprisingly good. A finer agreement between experiment and calculation necessitates a secular equation involving up to third- and fourth-neighbor interactions. For the calorimetric and x-ray data, which depend on an integration over the frequency spectrum, however, the first-neighbor model gives an adequate explanation of present observations.

ACKNOWLEDGMENTS

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[10] P. A. Flinn and A. A. Maradudin, Ann. Phys. (N.Y.) **22**, 223 (1963).

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