

Vibrational Spectrum of Sodium

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A five-term Houston's formula is used to calculate the vibrational spectrum of sodium on the basis of a three-force-constant model incorporating the electron gas modification as elaborated by Bhatia. From this spectrum the lattice specific heat is calculated and compared with the experimental data. The agreement between the present calculation and the experiment is more satisfactory than obtained by earlier workers.

INTRODUCTION

THE lattice vibrational spectrum is a quantity of considerable interest. The early theory of lattice vibrations developed by Born and von Kármán has been generalized and extended by many workers.^{1,2} In the general theory, the equations of motion of the atoms in a lattice are developed in terms of harmonic-interatomic tensor forces. Solutions of the equations of motion in terms of plane-wave normal coordinates lead to a secular equation relating the frequencies to the wave vectors of the travelling waves. An approximate frequency spectrum of the normal modes can be obtained from the secular equation by several methods.³⁻⁷ The formulation of an adequate model, i.e., finding the atomic-force constants for a calculation of the lattice vibrational properties of a metal, presents great difficulties because of the presence of conduction electrons. A number of models⁸⁻¹¹ have been put forward wherein the electron gas is considered and taken account of in various approximate ways. Bhatia, taking into account in a simple way the effect of valence electrons on the ionic motion in monovalent cubic metals, but considering only the interaction between the nearest neighbors, calculated the dispersion of the lattice waves, the frequency spectrum, and the specific heat of sodium. Sodium is a highly anisotropic substance and for this a three-term approximation, the one used by Houston and by Bhatia in their calculations, gives poor results.^{12,13} In their work on the evaluation of the equivalent Debye temperatures of fcc metals Horton and Schiff¹⁴ find that the use of more than five directions

is not required and proves unrewarding even for anisotropic substances like lead. For substances like silver [anisotropy factor $\eta = 2c_{44}/(c_{11} - c_{12}) = 3.0$], the five-term Θ_0 is 0.1% greater than a fifteen-term approximation. Θ_0 values from a 15-term approximation are in agreement within 1% with the values from numerical integration methods and also with the experimental values.¹⁵ From the calculations made in cases of highly anisotropic substances like lead ($\eta = 4.0$), lithium ($\eta = 7.8$), and sodium ($\eta = 8.2$), we find small differences between the values of Θ_0 from the five- and fifteen-term approximations; in the case of lead this difference is 0.2%, for lithium it is less than 0.1%, and for sodium it is 0.7%. In contrast with this, the values of Θ_0 from the three- and fifteen-term approximations in the cases of silver, lead, lithium, and sodium differ by 4, 7, 12, and 13%, respectively. This has prompted us to calculate the vibrational spectrum of sodium with a five-term approximation.

THEORY

The homogeneous linear equations for the components of the displacement vector of the lattice waves in a body-centered cubic metal may be written as¹¹

$$\lambda\rho\omega^2 = \sum_{l,m,n} \left\{ \frac{3}{4}a^{-2}[\sin^2(\frac{1}{2}ka(Ll + Mm + Nn))] \right. \\ \left. \times [(2c_{44} + \epsilon)\lambda - 3el(\lambda l + m\mu + n\nu)] \right\} \\ + \frac{(c_{11} - c_{44})L(\lambda L + \mu M + \nu N)k^2}{1 + (c_{11} - c_{44})(k^2/4\pi e^2 n_0^2)}, \quad (1)$$

and two similar equations obtained from (1) by interchanging (l, m, n) , (λ, μ, ν) and (L, M, N) as follows:

$$l \rightleftharpoons m, \quad \lambda \rightleftharpoons \mu, \quad \text{and} \quad L \rightleftharpoons M; \\ l \rightleftharpoons n, \quad \lambda \rightleftharpoons \nu, \quad \text{and} \quad L \rightleftharpoons N.$$

Here (L, M, N) and (λ, μ, ν) are the direction cosines of the propagation vector \mathbf{k} and of the displacement vector, respectively, c_{11} , c_{44} , and c_{12} are elastic constants, $\epsilon = c_{11} - c_{12} - 2c_{44}$, ρ is the density, n_0 the number of electrons per cm³, a the nearest-neighbor distance, (l, m, n) the direction cosines of the line joining the ion at the origin and the nearest-neighbor ions, and the summation in (1) is only over the nearest neighbors.

¹⁵ G. A. Alers and J. R. Neighbours, *Revs. Modern Phys.* **31**, 675 (1959).

¹ M. Blackman, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII, Pt. 1, p. 325.

² J. de Launay, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 219.

³ W. V. Houston, *Revs. Modern Phys.* **20**, 161 (1948).

⁴ R. B. Leighton, *Revs. Modern Phys.* **20**, 165 (1948).

⁵ E. W. Montroll, *J. Chem. Phys.* **10**, 218 (1942); **11**, 481 (1943); **12**, 98 (1944).

⁶ M. Lax and J. L. Lebowitz, *Phys. Rev.* **96**, 594 (1954).

⁷ J. C. Phillips, *Phys. Rev.* **104**, 1263 (1956); **113**, 147 (1959).

⁸ E. Bauer, *Phys. Rev.* **92**, 58 (1953).

⁹ G. Leibfried and W. Brenig, *Z. Physik* **134**, 451 (1953).

¹⁰ J. de Launay, *J. Chem. Phys.* **21**, 1975 (1953); **22**, 1676 (1954).

¹¹ A. B. Bhatia, *Phys. Rev.* **97**, 363 (1955).

¹² D. D. Betts, A. B. Bhatia, and M. Wyman, *Phys. Rev.* **104**, 37 (1956).

¹³ D. D. Betts, *Can. J. Phys.* **39**, 233 (1961).

¹⁴ G. K. Horton and H. Schiff, *Proc. Roy. Soc. (London)* **A250**, 248 (1959).

For brevity we shall call the directions [100], [110], [111], [210], and [211] the A , B , C , D , and E directions, respectively, and a subscript A , B , etc., on a symbol will imply its value in that direction. On solving the secular equation for \mathbf{k} lying in the directions A , B , C , D , and E , one finds the following expressions for ω^2 :

Direction A :

$$\omega^2 = (1/a^2\rho)[12c_{44}\sin^2(ka/2\sqrt{3}) + (c_{11}-c_{44})k^2a^2/(1+\phi k^2a^2)],$$

$$\omega^2 = (1/a^2\rho)12c_{44}\sin^2(ka/2\sqrt{3}).$$

Direction B :

$$\omega^2 = (1/a^2\rho)[(6c_{44}-3\epsilon)\sin^2(ka/\sqrt{6}) + (c_{11}-c_{44})k^2a^2/(1+\phi k^2a^2)],$$

$$\omega^2 = (1/a^2\rho)(6c_{44}+3\epsilon)\sin^2(ka/\sqrt{6}),$$

$$\omega^2 = (1/a^2\rho)6c_{44}\sin^2(ka/\sqrt{6}).$$

Direction C :

$$\omega^2 = (1/a^2\rho)[3(c_{44}-\epsilon)\sin^2(ka/2) + 3(3c_{44}+\epsilon)\sin^2(ka/6) + (c_{11}-c_{44})k^2a^2/(1+\phi k^2a^2)],$$

$$\omega^2 = (1/a^2\rho)[3(c_{44}+\frac{1}{2}\epsilon)\sin^2(ka/2) + 3(3c_{44}-\frac{1}{2}\epsilon)\sin^2(ka/6)].$$

Direction D :

$$\begin{aligned} \omega^2 &= (6c_{44}/a^2\rho)[\sin^2(3ka/2\sqrt{15}) + \sin^2(ka/2\sqrt{15})], \\ \omega_{\pm}^2 &= (1/a^2\rho)\{6c_{44}[\sin^2(3ka/2\sqrt{15}) + \sin^2(ka/2\sqrt{15})] \\ &\quad + (c_{11}-c_{44})k^2a^2/2(1+\phi k^2a^2)\} \\ &\quad \pm (1/a^2\rho)\{(c_{11}-c_{44})^2k^4a^4/4(1+\phi k^2a^2)^2 \\ &\quad + 9\epsilon^2[\sin^2(3ka/2\sqrt{15}) - \sin^2(ka/2\sqrt{15})]^2 \\ &\quad - (12/5)\epsilon(c_{11}-c_{44})k^2a^2/(1+\phi k^2a^2) \\ &\quad \times [\sin^2(3ka/2\sqrt{15}) - \sin^2(ka/2\sqrt{15})]\}^{1/2}. \end{aligned}$$

Direction E :

$$\begin{aligned} \omega^2 &= (1/a^2\rho)[3(c_{44}+\frac{1}{2}\epsilon)\sin^2(2ka/3\sqrt{2}) \\ &\quad + 6(c_{44}-\frac{1}{2}\epsilon)\sin^2(ka/3\sqrt{2})], \\ \omega_{\pm}^2 &= (1/a^2\rho)[3(c_{44}-\frac{1}{4}\epsilon)\sin^2(2ka/3\sqrt{2}) + 6(c_{44}+\frac{1}{4}\epsilon) \\ &\quad \times \sin^2(ka/3\sqrt{2}) + (c_{11}-c_{44})k^2a^2/2(1+\phi k^2a^2)] \\ &\quad \pm (1/a^2\rho)\{\frac{3}{4}\epsilon\sin^2(2ka/3\sqrt{2}) - \frac{3}{2}\epsilon\sin^2(ka/3\sqrt{2}) \\ &\quad + (c_{11}-c_{44})k^2a^2/6(1+\phi k^2a^2)\}^2 \\ &\quad + 2\{\frac{3}{2}\epsilon\sin^2(2ka/3\sqrt{2}) \\ &\quad - (c_{11}-c_{44})k^2a^2/3(1+\phi k^2a^2)\}^{1/2}. \quad (2) \end{aligned}$$

In Eq. (2) we have written

$$\phi a^2 = (c_{11}-c_{44})/4\pi e^2 n_0^2. \quad (3)$$

The frequency distribution function $G(\omega)$ gives the number of frequencies between ω and $\omega+d\omega$ per unit volume. Following Houston's method,^{3,12} the five-term approximation leads to the following expression for

$G(\omega)$:

$$\begin{aligned} G(\omega) &= \frac{F}{(2\pi)^3} \frac{4\pi}{10395} \sum_i \left[1197k^2 \left(\frac{dk}{d\omega} \right)_{i,A} + 1456k^2 \left(\frac{dk}{d\omega} \right)_{i,B} \right. \\ &\quad \left. + 729k^2 \left(\frac{dk}{d\omega} \right)_{i,C} + 3125k^2 \left(\frac{dk}{d\omega} \right)_{i,D} \right. \\ &\quad \left. + 3888k^2 \left(\frac{dk}{d\omega} \right)_{i,E} \right], \quad (4) \end{aligned}$$

where the summation is over the three solutions, which the secular equation has for each \mathbf{k} and F is the normalization factor to be chosen such that

$$\int_0^{\omega_{\max}} G(\omega) d\omega = 3N_0, \quad (5)$$

N_0 being the number of atoms per unit volume in the crystal. If we denote the maximum value of k along the directions A , B , etc., by $k_A(m)$, $k_B(m)$, etc., respectively, the normalization factor is determined by the equation

$$\begin{aligned} \frac{F}{(2\pi)^3} \frac{4\pi}{10395} [1197k_A^3(m) + 1456k_B^3(m) + 729k_C^3(m) \\ + 3125k_D^3(m) + 3888k_E^3(m)] = 3N_0. \quad (6) \end{aligned}$$

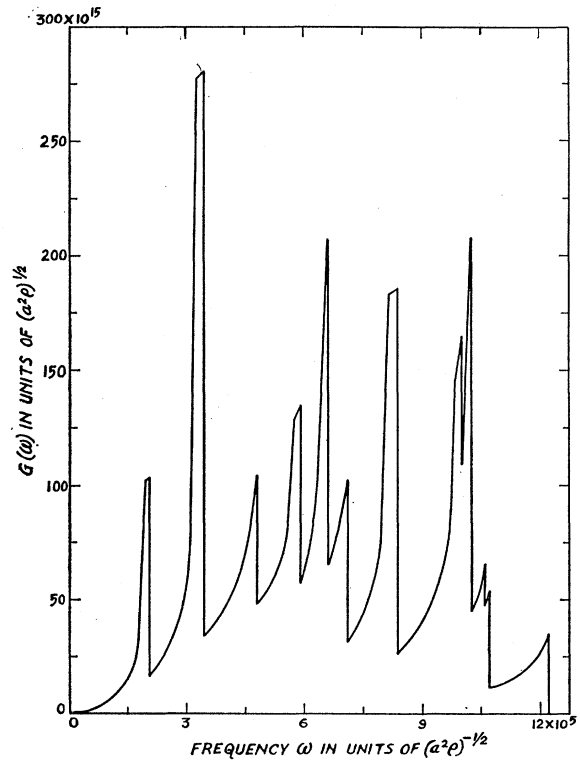


FIG. 1. The lattice vibrational spectrum of sodium.

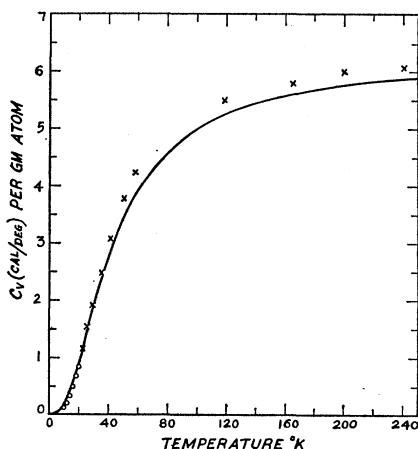


FIG. 2. The specific heat of sodium at different temperatures. The solid line is for the values calculated from the frequency spectrum. The crosses represent the experimental measurements of Simon and Zeidler. The circles denote the measured values due to Roberts.

For a body-centered cubic structure we find

$$k_A(m) = \sqrt{3}(\pi/a), \quad k_B(m) = (\frac{3}{2})^{\frac{1}{2}}(\pi/a), \quad k_C(m) = \frac{3}{2}(\pi/a), \\ k_D(m) = (5/3)^{\frac{1}{2}}(\pi/a), \quad k_E(m) = \sqrt{2}(\pi/a). \quad (7)$$

Equations (6) and (7) give

$$F = 0.886. \quad (8)$$

The frequency distribution function is now obtained in a straightforward manner with the help of (4), (8), and (2). Since there are usually critical points along the symmetry directions,^{7,16} Houston's method introduces spurious one-dimensional singularities into the distribution at frequencies where the correct distribution has corners. We have replaced the singularities in $G(\omega)$ by finite peaks of equal area.

RESULTS AND DISCUSSION

The values of the elastic constants needed in the calculation as well as the other constants used in the calculation are listed below:

$$c_{11} = 0.972 \times 10^{11} \text{ dynes/cm}^2, \\ c_{12} = 0.831 \times 10^{11} \text{ dynes/cm}^2, \\ c_{44} = 0.580 \times 10^{11} \text{ dynes/cm}^2.$$

$a = 3.715 \text{ \AA}$ and $\rho = 0.97 \text{ g cm}^{-3}$. The values of the elastic constants are the same as employed by Bhatia. The frequency distribution is shown in Fig. 1. Having obtained the frequency distribution, we are in a position to calculate the gram atomic specific heat C_v . This is obtained from the usual formula:

$$C_v = K \int_0^{\omega_m} G(\omega) E(\omega, T) d\omega. \quad (9)$$

¹⁶ L. Van Hove, Phys. Rev. **89**, 1189 (1953).

Here

$$E(\omega, T) = (\hbar\omega/KT)^2 \exp(\hbar\omega/KT) / [\exp(\hbar\omega/KT) - 1]^2,$$

R is the gas constant, \hbar is Planck's constant divided by 2π , and K is the Boltzmann constant. The integration was carried out numerically. The calculated and the experimental values are plotted in Fig. 2. The results of the entire numerical work of the present work are estimated to be correct within 2%. The experimental values of C_v above 20°K are due to Simon and Zeidler¹⁷ and those below 20°K are due to Roberts.¹⁸ The experimental C_v at lower temperatures are corrected for the electronic contribution. The calculated values at higher temperatures are systematically lower than the experimental ones. In Fig. 3, the more sensitive plots of Θ vs T are given for (a) the values of Θ derived from the specific heat calculated in the present paper, (b) Θ values obtained by Bhatia from the three-term approximation, (c) Θ 's obtained by Bauer⁸ using a two-force-constant model with interactions taken up to second-nearest neighbors and also Houston's three-term approximation, and finally (d) the values of Θ calculated by Dayal and Sharan¹⁹ based on the three-force-constant model of de Launay,^{2,10} who assumes a central force connecting the nearest and next-nearest neighbor atoms, and a force arising from the compressibility of the electron gas. Dayal and Sharan use the sampling method to compute the frequency spectrum. All these workers use the same set of elastic constants, as used in the present work, a fact which makes the inter-comparison of their results meaningful.

It is seen from Fig. 3 that the agreement between the calculated and observed values of Θ is satisfactory at

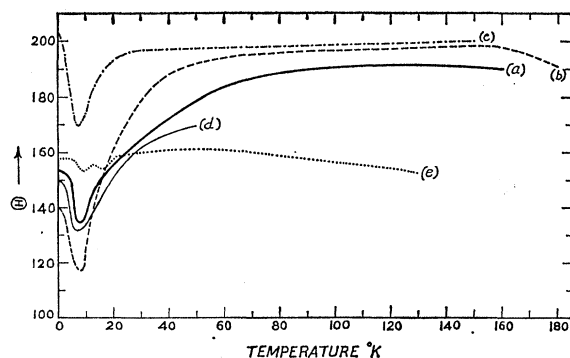


FIG. 3. Debye characteristic temperature Θ as a function of temperature. Curve (a) represents the results of the present calculation, curve (b) indicates the values from Bhatia's calculation, curve (c) shows the values of Θ calculated by Bauer, and curve (d) reproduces the theoretical results of Dayal and Sharan. Curve (e) corresponds to the experimental measurements.

¹⁷ F. E. Simon and W. Zeidler, Z. physik. Chem. **B123**, 383 (1926).

¹⁸ L. M. Roberts, Proc. Phys. Soc. (London) **70**, 744 (1957).

¹⁹ B. Dayal and B. Sharan, Proc. Roy. Soc. (London) **A262**, 136 (1961).

low temperatures. Our calculated curve (a) is nearer the experimental values than the curves obtained by other workers mentioned above. At higher temperatures there is an increasing discrepancy between the theoretical values and the experimental ones. At these temperatures the specific heat is less sensitive to the details of the frequency spectrum, and a small change in the specific heat requires a large change in Θ . A possible explanation of the effect lies in the anharmonic correction. In principle, of course, to obtain the specific heat at a given temperature, the frequency distribution at that temperature should be used. We should mention, however, that these discrepancies between the theory and the experiment may be partly due to the inadequacy of the assumptions on which the secular equation was derived, and the approximate method of calculating the frequency spectrum. Recent experiments on both the diffuse x-ray scattering and the inelastic scattering of cold neutrons by lattice vibrations suggest that atoms beyond first-neighbors interact appreciably. In addition the transformation of a martensitic type occurring in

sodium²⁰⁻²² around 40°K produces a variation in the experimental results and will affect our comparison. Sodium changes from a high-temperature body-centered structure to a low-temperature hexagonal close-packed structure with a c/a ratio equal to the ideal value of 1.63, and at very low temperatures near absolute zero a sample of sodium will consist of a mixture of two phases. Only the high-temperature bcc phase approximates a free electron gas model. Therefore, for comparison with our theory, measurements on a sample in which the transformation to the low-temperature phase has somehow been inhibited would be desirable.

ACKNOWLEDGMENTS

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²⁰ C. S. Barrett, *Acta Cryst.* **9**, 671 (1956).

²¹ D. L. Martin, *Proc. Roy. Soc. (London)* **A254**, 433 (1960).

²² E. A. Stern, *Phys. Rev.* **121**, 397 (1961).