

## The Normal Modes of Vibration of a Body-Centered Cubic Lattice

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An atomic model is set up for the purpose of finding the normal modes of vibration of a body-centered cubic lattice. A method is presented for selecting suitable atomic force constants from the macroscopic elastic properties of tungsten, which satisfy the isotropy condition but not the Cauchy relation. Actual solutions of the secular equation are then carried out under the assumption that each atom is affected by only its fourteen nearest neighbors. Numerical computations yield a frequency distribution characterized by two steep maxima. This is used in evaluating the specific heat and the intensity of reflection of x-rays as functions of temperature, and the results are compared with the Debye theory.

VARIOUS models have been proposed for the description of solid bodies and the consequences worked out in more or less detail. One of the most productive theories was formulated by Debye,<sup>1</sup> who considered a solid as an isotropic continuum, found that the number of vibrations in a given frequency range was proportional to the square of the frequency, and investigated the thermal variation of specific heats and the intensity of reflection of x-rays. At first the results were thought to be in very good agreement with experiment but discrepancies soon appeared. Several attempts have been made to explain these deviations by regarding a crystal as an atomic lattice rather than a continuum. Born and v. Kármán<sup>2</sup> derived an approximate expression for the specific heat by considering a simple cubic lattice. The general theory of atomic vibrations has been discussed by Born<sup>3</sup> and applied to two-dimensional lattices and polar crystals by Blackman.<sup>4</sup> In the present work an actual numerical calculation of the frequency distribution has been carried out for a model related to tungsten, a body-centered cubic crystal with elastic constants which happen to satisfy the isotropy condition.

The potential energy of the lattice is to a first approximation a quadratic function of the displacements of the atoms from their equilibrium positions. Let  $u_{\mathbf{r}}^j$  denote the component in the  $j$ th

coordinate direction of the displacement of the atom whose lattice position is specified by the vector  $\mathbf{r}$ . Suppose that the potential energy  $V$  is expanded in a power series in terms of the displacements. Then,

$$V = V_0 + \sum_j \sum_{\mathbf{r}} (\partial V / \partial u_{\mathbf{r}}^j)_0 u_{\mathbf{r}}^j + (\frac{1}{2}) \sum_j \sum_k \sum_{\mathbf{r}} \sum_{\mathbf{r}'} (\partial^2 V / \partial u_{\mathbf{r}}^j \partial u_{\mathbf{r}'}^k)_0 u_{\mathbf{r}}^j u_{\mathbf{r}'}^k + \dots \quad (1)$$

The summations with respect to  $\mathbf{r}$  and  $\mathbf{r}'$  are taken over all the atoms in the crystal and the superscripts  $j$  and  $k$  are summed over the three coordinate directions. The derivatives are to be evaluated when the displacements are all zero. The force in the  $j$  direction on the atom with a lattice position specified by  $\mathbf{r}$  is  $(\partial V / \partial u_{\mathbf{r}}^j)_0$  when all other atoms are also in their lattice positions, and this force must vanish since the solid is then in equilibrium. If  $V_0$  is taken as the zero reference value for the potential energy, then

$$V = (\frac{1}{2}) \sum_j \sum_k \sum_{\mathbf{r}} \sum_{\mathbf{r}'} C_{jk}^{\mathbf{r}\mathbf{r}'} u_{\mathbf{r}}^j u_{\mathbf{r}'}^k, \quad (2)$$

where

$$C_{jk}^{\mathbf{r}\mathbf{r}'} = (\partial^2 V / \partial u_{\mathbf{r}}^j \partial u_{\mathbf{r}'}^k)_0.$$

Higher order terms are neglected for displacements small compared with the distances between atoms. By definition,

$$C_{jk}^{\mathbf{r}\mathbf{r}'} = C_{kj}^{\mathbf{r}'\mathbf{r}},$$

because both constants are factors of the same displacement product,  $u_{\mathbf{r}}^j u_{\mathbf{r}'}^k$ . For a monatomic cubic lattice, where every atom is situated in exactly the same way with respect to its

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<sup>1</sup> P. Debye, *Ann. d. Physik* **39**, 789 (1912); **43**, 49 (1914).

<sup>2</sup> M. Born and Th. v. Kármán, *Physik. Zeits.* **13**, 297 (1912); **14**, 15 (1913).

<sup>3</sup> M. Born, *Atomtheorie des festen Zustandes* (Berlin, 1923).

<sup>4</sup> M. Blackman, *Proc. Roy. Soc.* **A148**, 365 (1935); *Phil. Trans. Roy. Soc.* **A236**, 103 (1936).

neighbors, there is an additional relation,

$$C_{kj}^{\mathbf{r}\mathbf{r}'} = C_{jk}^{\mathbf{r}'\mathbf{r}} = C_{jk}^{\mathbf{r}'-\mathbf{r}}, \quad (3)$$

so that the atomic force constants are symmetrical in their subscripts and depend only on the difference in the lattice positions of the atoms involved.

The kinetic energy of the atoms in the crystal can be written as

$$T = (\frac{1}{2})m \sum_j \sum_{\mathbf{r}} (\dot{u}_{\mathbf{r}}^j)^2, \quad (4)$$

where  $m$  is the mass of the atom and  $\dot{u}_{\mathbf{r}}^j$  is the time derivative of the displacement. The problem is to reduce the potential energy to a simpler form by introducing normal coordinates without thereby complicating the kinetic energy expression. This can be done for a general translation lattice but only the special case of a body-centered cubic crystal will be considered here. The basic cell then consists of two atoms, one situated at the point  $(0, 0, 0)$  and the other at  $(a/2, a/2, a/2)$ , where  $a$  is the length of one edge of the basic cube. The lattice position of any atom in the crystal is given either by  $r_j = q_j a$  or by  $r_j = (q_j + \frac{1}{2})a$ , the integer  $q_j$  having values which range from zero to  $N_j$ , the total number of cells along the  $j$ th axis of the crystal.

The displacement of each atom is regarded as resulting from the superposition of plane waves in the solid, so that

$$u_{\mathbf{r}}^j = \sum_n \{ w_{0, n}^j \exp [2\pi i \sum_j (n_j q_j / N_j)] + w_{\frac{1}{2}, n}^j \exp [2\pi i \sum_j n_j (q_j + \frac{1}{2}) / N_j] \}, \quad (5)$$

where  $n_j$  is an integer related to the direction of the wave and having values from  $-(\frac{1}{2})(N_j - 1)$  to  $(\frac{1}{2})(N_j - 1)$ . For the right side of this equation to be real, it is necessary that the normal coordinates  $w_{0, n}^j$  and  $w_{\frac{1}{2}, n}^j$  be complex and that  $w_{0, -n}^j = w_{0, n}^{j*}$  and  $w_{\frac{1}{2}, -n}^j = w_{\frac{1}{2}, n}^{j*}$ . The number of independent coordinates is therefore equal to the number of degrees of freedom of the atoms in the crystal.

When this change of variables is made in the potential energy, the result is

$$V = (\frac{1}{2})N_1 N_2 N_3 \sum_j \sum_k \sum_n [C_{jk}^n (w_{0, n}^j w_{0, -n}^k + w_{\frac{1}{2}, n}^j w_{\frac{1}{2}, -n}^k) + 2C_{jk}^{n'} w_{0, n}^j w_{\frac{1}{2}, -n}^k], \quad (6)$$

where

$$C_{jk}^n = \sum_g C_{jk}^g \exp [-2\pi i \sum_j (n_j g_j / N_j)]$$

and

$$C_{jk}^{n'} = \sum_g C_{jk}^{g+\frac{1}{2}} \exp [-2\pi i \sum_j n_j (g_j + \frac{1}{2}) / N_j].$$

The quantity  $g_j$  is equal to  $q_j' - q_j$  and the summation is from  $g_j = -(N_j - 1)$  to  $g_j = (N_j - 1)$ . The kinetic energy has the following form after reduction:

$$T = (\frac{1}{2})N_1 N_2 N_3 m \sum_j \sum_n \left[ \left( \frac{\partial w_{0, n}^j}{\partial t} \right) \left( \frac{\partial w_{0, -n}^j}{\partial t} \right) + \left( \frac{\partial w_{\frac{1}{2}, n}^j}{\partial t} \right) \left( \frac{\partial w_{\frac{1}{2}, -n}^j}{\partial t} \right) \right], \quad (7)$$

The equations of motion found by Lagrange's method are then

$$\sum_j (C_{jk}^n w_{0, n}^j + C_{jk}^{n'} w_{\frac{1}{2}, n}^j) = m \frac{\partial^2 w_{0, n}^k}{\partial t^2}, \quad (8)$$

$$\sum_j (C_{jk}^{n'} w_{0, n}^j + C_{jk}^n w_{\frac{1}{2}, n}^j) = m \frac{\partial^2 w_{\frac{1}{2}, n}^k}{\partial t^2}.$$

If now it is assumed that

$$w_{0, n}^j = A_{0, n}^j \exp [i\omega_n t]$$

and

$$w_{\frac{1}{2}, n}^j = A_{\frac{1}{2}, n}^j \exp [i\omega_n t]$$

where  $\omega_n$  is proportional to the frequency of vibration, homogeneous linear equations are obtained for the unknown amplitudes. The condition for a nontrivial solution is a sixth-order determinant set equal to zero. However, two third-order factors can be found and the two determinantal equations written together in the form,

$$\begin{vmatrix} (C_{11}^n \pm C_{11}^{n'} - m\omega_n^2) & (C_{12}^n \pm C_{12}^{n'}) & (C_{13}^n \pm C_{13}^{n'}) \\ (C_{12}^n \pm C_{12}^{n'}) & (C_{22}^n \pm C_{22}^{n'} - m\omega_n^2) & (C_{23}^n \pm C_{23}^{n'}) \\ (C_{13}^n \pm C_{13}^{n'}) & (C_{23}^n \pm C_{23}^{n'}) & (C_{33}^n \pm C_{33}^{n'} - m\omega_n^2) \end{vmatrix} = 0. \quad (9)$$

The positive sign gives one equation and the negative sign another.

There is a frequency for every value of  $n$  so that a whole spectrum is obtained. For certain special directions in the crystal the determinant can be reduced to linear or quadratic factors and explicit solutions obtained immediately, but in general numerical methods must be used in solving the cubic equations. This necessitates information about the values of the atomic constants involved. By equating the potential energy arising from a large scale distortion of the solid to that resulting from the corresponding atomic displacements it is possible to secure relations between the atomic force constants and the macroscopic elastic properties of the crystal. However, these are not sufficient to determine the atomic constants uniquely unless simplifying assumptions are made. Thus, for the body-centered cubic lattice, only the interactions between a given atom and its fourteen nearest neighbors will be considered. After the symmetry properties of the crystal are utilized, only five atomic force constants remain and these are related to the macroscopic elastic constants,  $c_{11}$ ,  $c_{12}$  and  $c_{44}$ , by the following equations:

$$\begin{aligned} C_{11}^{0,0,0} + 2C_{11}^{1,0,0} + 4C_{11}^{0,1,0} + 8C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= 0, \\ C_{11}^{1,0,0} + C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= -\left(\frac{1}{2}\right)ac_{11}, \\ C_{11}^{0,1,0} + C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= -\left(\frac{1}{2}\right)ac_{44}, \\ C_{12}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= -\left(\frac{1}{2}\right)ac_{12}. \end{aligned} \quad (10)$$

The superscripts refer to the difference in lattice positions for the atoms concerned.

If central forces are postulated,  $C_{11}^{0,1,0}$  may be neglected, since a displacement at right angles to the line connecting two atoms gives rise to a second-order effect in the potential energy. Moreover, the model used leads to the Cauchy rela-

tions, which state that  $c_{12} = c_{44}$  for a cubic crystal. This relation is not experimentally verified for metals, so that some modification is necessary in order to obtain suitable atomic constants from empirical data. A way of doing this is suggested by the work of Fuchs,<sup>5</sup> who showed by means of the Wigner-Seitz quantum-mechanical methods that the failure of the Cauchy relation for a monovalent metal is due to the effect of the valence electrons on the compressibility of the crystal. The constants  $c_{44}$  and  $c_{11} - c_{12}$  are not affected because they are involved in strains where the volume is not changed. Since, in the present work, the atom is represented as a point mass and no provision is made for the electrons, it seems reasonable in securing appropriate force constants to make use of the Cauchy relation as the third condition instead of the observed compressibility.

The experimental values<sup>6</sup> for the elastic constants of a tungsten single crystal at room temperature are as follows:

$$\begin{aligned} c_{11} &= 5.13 \times 10^{12} \text{ dynes/cm}^2, \\ c_{12} &= 2.06 \times 10^{12}, \\ c_{44} &= 1.53 \times 10^{12}. \end{aligned} \quad (11)$$

The isotropy condition,  $c_{44} = (\frac{1}{2})(c_{11} - c_{12})$ , is therefore satisfied<sup>7</sup> and the equations for the atomic force constants can be solved.

$$\begin{aligned} C_{11}^{0,0,0} &= 6ac_{44}, \\ C_{11}^{1,0,0} &= -ac_{44}, \\ C_{11}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= C_{12}^{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = -\left(\frac{1}{2}\right)ac_{44}. \end{aligned} \quad (12)$$

Without isotropy the atomic constants would be expressed in terms of two parameters instead of the single one appearing here. The sums which enter the secular equation (9) may now be evaluated and the determinant written out as follows:

$$\begin{vmatrix} (1 + \sin^2 x \mp \cos x \cos y \cos z - f_n^2) & (\pm \sin x \sin y \cos z) & (\pm \sin x \cos y \sin z) \\ (\pm \sin x \sin y \cos z) & (1 + \sin^2 y \mp \cos x \cos y \cos z - f_n^2) & (\pm \cos x \sin y \sin z) \\ (\pm \sin x \cos y \sin z) & (\pm \cos x \sin y \sin z) & (1 + \sin^2 z \mp \cos x \cos y \cos z - f_n^2) \end{vmatrix} = 0. \quad (13)$$

Here,  $x = \pi n_1/N_1$ ,  $y = \pi n_2/N_2$ ,  $z = \pi n_3/N_3$ , and  $f_n = (m\omega_n^2/4ac_{44})^{\frac{1}{2}}$ , a quantity directly proportional to the frequency.

In order to find the values of  $f_n^2$  at various points in ten planes perpendicular to the  $z$  axis,

140 cubic equations were solved. Then, by interpolation, curves of constant frequency in these

<sup>5</sup> K. Fuchs, Proc. Roy. Soc. **A153**, 622 (1936); **157**, 444 (1936).

<sup>6</sup> P. W. Bridgman, Proc. Nat. Acad. **10**, 411 (1924).

<sup>7</sup> S. J. Wright, Proc. Roy. Soc. **A126**, 613 (1930).

planes were determined, their areas found numerically, and the volumes bounded by surfaces of constant frequency built up out of these

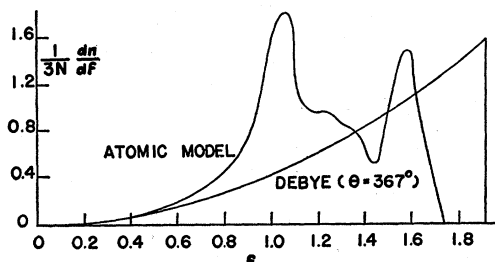


FIG. 1. Frequency distribution.

slices. This gives the number of modes of vibration having a frequency less than a certain value and may be designated by  $n$ . To obtain the frequency distribution an approximate differentiation was performed and the curve in Fig. 1 secured for  $(1/3N)(dn/df)$ , a quantity equal to the fraction of the total number of vibrations in a given frequency range.  $N$  is equal to  $2N_1N_2N_3$ , the total number of atoms in the lattice.

It is found that at very low frequencies the Debye type of distribution is valid, a result to be expected when the wave-length is long in comparison with interatomic dimensions. A parabolic extension of this part of the curve gives a Debye function with a characteristic temperature  $\theta=367^\circ$ , agreeing closely with the value of  $373^\circ$  calculated from the elastic constants by means of the Debye theoretical formula. However, it is clear that there is agreement between the two curves only over an insignificant portion of the complete spectrum. The most distinctive feature of the distribution for the atomic model is the presence of two steep maxima. This is to some extent a justification of the Nernst-Lindemann specific heat formula where two frequencies are utilized instead of the single frequency of the Einstein theory. Another difference between the distributions for the atomic model and the Debye theory is in the determination of the upper limit of the frequency. According to Debye, the distribution derived for a continuum is abruptly terminated at a point where the number of vibrations equals the number of degrees of freedom of the atoms in the solid. This sudden use of the atomicity of

the crystal as a last resort is artificial and contradictory. In the present work where the atomic nature of the solid is considered from the beginning, the existence of a maximum frequency is a natural and necessary consequence.

One of the applications of the frequency distribution is in computing the specific heat at constant volume, which can be written in the form,

$$C_v = \int_0^{\nu_m} \frac{(h^2\nu^2/kT^2)(e^{h\nu/kT})}{(e^{h\nu/kT}-1)^2} (dn/d\nu) d\nu. \quad (14)$$

A numerical integration has been carried out for the atomic model, and the comparison between theory and experiment is shown in Table I. The Debye values for  $\theta=310^\circ$  are the result of fitting the empirical data for tungsten. The fact that the Debye characteristic temperature is often selected to give the best fit with the observed specific heats instead of being calculated from the theoretical formula involving the elastic constants is perhaps a cause of undue confidence in the theory. Although the present work also gives a specific heat which depends on a single constant, it was not thought advisable to evaluate it from observations which include the effect of electrons as well as atomic vibrations and probably interactions between the two.

It is seen that the Debye values for  $\theta=367^\circ$  are too low at all temperatures, while those for  $\theta=310^\circ$  are in very good agreement with experiment. The atomic model and the Debye theory

TABLE I. Specific heats (cal. per mole per  $^\circ K$ ).

$T$	$C_v$ (ATOMIC MODEL)	$C_v$ (OBS.)*	$C_v$ (DEBYE, $\theta=367^\circ$ )	$C_v$ (DEBYE, $\theta=310^\circ$ )
26.01° K	0.242	0.213	0.165	0.272
32.3	0.495	0.434	0.310	0.506
38.8	0.842	0.750	0.528	0.826
46.7	1.34	1.21	0.861	1.28
54.7	1.84	1.80	1.25	1.77
74.4	2.94	2.87	2.25	2.85
78.3	3.12	3.07	2.42	3.03
84.2	3.37	3.33	2.69	3.29
91.1	3.63	3.60	2.97	3.55
100	3.92	3.77	3.30	3.85
150	4.90		4.50	4.86
200	5.32	5.30	5.06	5.30
250	5.52		5.36	5.52
300	5.66	5.87	5.54	5.65

\* F. Lange, Zeits. f. physik. Chemie 110, 343 (1924). (For temperatures from 26.01 to 91.1.) C. Zwicker, Zeits. f. Physik 52, 668 (1928). (For temperatures from 100 to 300.)

TABLE II. Root mean square displacements.

$T$	$\mu^{\frac{1}{2}}$ (ATOMIC MODEL)	$\mu^{\frac{1}{2}}$ (DEBYE, $\theta = 367^\circ$ )	$\mu^{\frac{1}{2}}$ (DEBYE, $\theta = 310^\circ$ )
0°K	0.0251A	0.0231A	0.0251A
100	0.0307	0.0279	0.0319
200	0.0401	0.0356	0.0417
300	0.0480	0.0426	0.0502
400	0.0550	0.0488	0.0576
500	0.0613	0.0544	0.0642

have in common the variation of the specific heat as the third power of the temperature near absolute zero and the asymptotic approach to the equipartition value at high temperatures. The specific heat for the atomic model checks very well with the empirical data at intermediate temperatures, but the results are too high at low temperatures. This is probably due in part to the fact that it was necessary to use elastic constants which had been measured at room temperature. An increase in the elastic constants as the temperature is lowered would lead to a smaller specific heat. Although no information is available for tungsten, metals with similar crystal structures do have elastic properties which behave in such a way. On the other hand, the rise of the observed specific heat above the equipartition value at high temperatures may be caused in part by anharmonic vibrations which are responsible for the thermal expansion of the solid and in part by the excitation of electronic motions.

Another application deals with the variation of the intensity of reflection of x-rays with temperature. The theory was first developed by Debye and has been put in more concise form by Zener and Jauncey.<sup>8</sup> Because of their thermal motion the atoms do not remain in the lattice planes but undergo displacements which increase with the temperature and result in destructive interference and lower intensity for the reflected x-rays. The temperature factor may be written as  $e^{-M}$ , where

$$M = (8\pi^2\mu \sin^2 \varphi) / \lambda^2, \tag{15}$$

<sup>8</sup> C. Zener and G. E. M. Jauncey, Phys. Rev. **49**, 17 (1936); C. Zener, Phys. Rev. **49**, 122 (1936).

$\varphi$  being the grazing angle of incidence,  $\lambda$  the wave-length, and  $\mu$  the mean square displacement of an atom from a given plane. For a cubic crystal  $\mu$  has the same value for all planes and is given by the following expression:

$$\mu = (h/12\pi^2Nm) \int_0^{\nu_m} (1/\nu) \times \{ [1/(e^{h\nu/kT} - 1)] + \frac{1}{2} \} (dn/d\nu) d\nu, \tag{16}$$

where  $\nu_m$  is the maximum frequency. This integral has also been evaluated numerically for the atomic model and the results are compared with the Debye theory in Table II, where the root mean square displacements are given in angstroms.

At high temperatures the theoretical formula for  $\mu$  is particularly simple and significant, showing a linear temperature variation with a slope equal to the average value of the reciprocal of the square of the frequency with respect to the frequency distribution.

Atomic model:

$$\mu = (6.28 + 0.0742T) \times 10^{-20} \text{ cm}^2$$

Debye ( $\theta = 367^\circ$ ):

$$\mu = (5.34 + 0.0583T) \times 10^{-20} \tag{17}$$

Debye ( $\theta = 310^\circ$ ):

$$\mu = (6.32 + 0.0815T) \times 10^{-20}.$$

Thus, the various theories give different values for the intensity of x-ray reflections at high temperatures, although the specific heats all agree in approaching the equipartition value. However, it is not possible at present to compare these results with experiment since there are no data available for tungsten.

It is hoped that this work may be continued by applications to other body-centered cubic lattices and also to face-centered cubic crystals. The numerical difficulties increase with the complexity of the crystal structure and a less complicated method of obtaining the frequency distribution from the secular equation would be desirable.

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