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The theory of the specific heat of a body centered cubic lattice

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THE THEORY OF THE SPECIFIC HEAT OF A BODY CENTERED CUBIC LATTICE

BY

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C. C. W.

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INTRODUCTION

In normal crystalline solids the atoms are at rest in their lattice points at absolute zero of temperature. Increasing the temperature of the crystal increases the motion of the atoms about their lattice points. Approximately, each atom or ion may be treated as a harmonic oscillator. Then from the equations of motion of the atoms, by the Born-von Kármán theory of specific heats, the normal modes of vibration of the lattice can be expressed as the roots of a secular determinant.

Application of this theory to determine the thermodynamic properties of crystals has resulted either in solutions that are inaccurate because of oversimplification or in cumbersome accurate solutions. Moreover, all the solutions tend to fail with decreasing temperature.

The purpose of this paper is to obtain the specific heat of a body-centered cubic crystal as a function of the absolute temperature, treating each atom as a harmonic oscillator vibrating about its lattice point. It is hoped that this method will show how the specific heat changes with temperature.

REVIEW OF LITERATURE

Since Classical Theory cannot satisfactorily explain the decrease in specific heat at low temperatures, Einstein[1]

(1) Seitz, F., The Modern Theory of Solids, McGraw-Hill, pp. 103 - 117, 1940.

postulated that a crystal might be regarded as being made up of harmonic oscillators. However, in his model all the oscillators had the same frequency. This assumption of a single frequency caused the theoretical specific heat to decrease too rapidly at low temperatures.

Then Debye[2] proposed an elastic-continuum model of a

(2) Seitz, F., The Modern Theory of Solids, McGraw-Hill, pp. 104 - 117, 1940

crystal, which led to a range of frequencies for the harmonic oscillators---the so-called normal modes of vibration of the crystal. His theory agreed well with experiment except for one important point: it predicted a constant for each crystal, the Debye characteristic temperature. Later it was found that this constant actually varies with temperature, especially at low temperatures.

Finally Born and von Kármán[3] proposed the modern lattice-

(3) Seitz, F., The Modern Theory of Solids, McGraw-Hill, pp. 118 - 123, 1940

theory of specific heats; although physically satisfactory,

mathematically it has great difficulties.

Blackman[4] has investigated the difference between the

(4) Blackman, M., Theory of the Specific Heat of Crystals, Proc. Roy. Soc., Vol. 148, pp. 365 - 406, (1935)

Debye or continuum theory and the Born-von Kármán or lattice theory. The density of vibrations as it affects many of the properties of crystals is discussed quite extensively.

Blackman[5] calculated the vibrational spectrum of a simple

(5) Blackman, M., On the Vibrational Spectrum of a Three Dimensional Lattice, Proc. Roy. Soc., Vol. 159, p. 116, (1937)

cubic lattice with the Born-von Kármán theory by a numerical method.

Fine[6] has also applied this theory to calculate the

(6) Fine, P. C., The Normal Modes of Vibration of a Body-Centered Cubic Lattice, Phys. Rev., Vol. 56, p. 335, (1939)

normal modes of vibration, using the Cauchy relations between the elastic constants, and compared the results with the data for some body-centered cubic crystals.

Leighton[7] obtained a secular determinant from the equa-

(7) Leighton, R. B., The Vibrational Spectrum and Specific Heat of a Face-Centered Cubic Crystal, Rev. of Mod. Phys., Vol. 20, p. 165, (1948)

tions of motion of atoms about their lattice sites and used

the force constants determined by K. Fuchs[8] to calculate

(8) Fuchs, K., A Quantum Mechanical Calculation of the Elastic Constants of Monovalent Metals, Proc. Roy. Soc., Vol. 153, p. 622, (1936)

the specific heat of some face-centered cubic crystals.

Montroll developed an elaborate method for calculating the frequency distribution of the square lattice and simple cubic lattice[9] and the body-centered cubic lattice.[10]

(9) Montroll, E. W., Frequency Spectrum of Crystalline Solids, Jour. Chem. Phys., Vol. 10, pp. 218 - 229, (1942)

Montroll, E. W., Frequency Spectrum of Crystalline Solids, II. General Theory and Applications to Simple Cubic Lattice, Jour. Chem. Phys., Vol. 11, pp. 481 - 495, (1943)

(10) Montroll, E. W. and Peaslee, D. C., Frequency Spectrum of Crystalline Solids, III. Body Centered Cubic Lattice, Jour. Chem. Phys., Vol. 12, pp. 98 - 106, (1944)

However, the series he developed do not converge at low temperatures.

In applying the Born-von Kármán theory to a crystal the Brillouin Zone[11] of its lattice is needed. First the

(11) Brillouin, L., Wave Propagation in Periodic Structures, McGraw-Hill, pp. 94 - 139, 1946

reciprocal lattice is obtained from the direct lattice and then planes, which are perpendicular bisectors of the basis vectors of the reciprocal lattice, are drawn to form the zone.

THE SQUARE LATTICE

The simplest and the easiest of all lattices to comprehend is the simple square lattice. Consider each lattice point as occupied by an atom free to vibrate in a plane within the restrictions of the forces between atoms. Later the generalization to a more complex structure will be easier.

Consider $\vec{d}_1$ and $\vec{d}_2$ as the basis vectors drawn from the lattice site chosen as the origin. The vector coördinate of any point in the lattice may then be expressed by

(1) $$\vec{R} = \ell \vec{d}_1 + m \vec{d}_2$$

where ℓ and m are integers. Using this direct lattice, we can obtain the equations of motion and periodicity of the substance. The frequency of vibration must be obtained so the direct lattice will first be used. After obtaining the equations of motion, we consider the wave vector in reciprocal space and use the reciprocal lattice. In Fig. 2 the reciprocal lattice points are represented by dots.

In order to remove any ambiguities in the wave length and direction of propagation we shall zone the reciprocal lattice. The zone is bounded by perpendicular bisectors of the basis vectors of the reciprocal lattice. In Fig. 3 the zone (called the first Brillouin Zone) is bounded by straight lines in the reciprocal square lattice.

The zone includes a complete period for each direction of propagation. It includes all allowable frequencies.

The Square Lattice

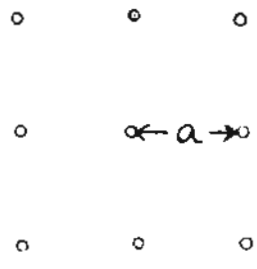

Fig. 1.

The Reciprocal of the Square Lattice.

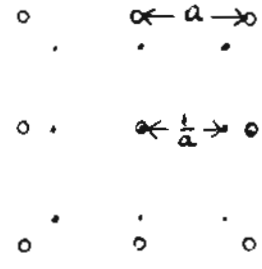

Fig. 2.

The First Brillouin Zone of the Square Lattice.

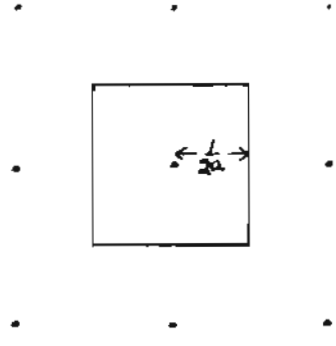

Fig. 3.

Consider only the nearest and next nearest neighbors where u and v denote displacements in the x and y directions, respectively, and ℓ and m (integers) denote coordinates in these directions with respect to any chosen lattice point.

Displacing the atoms in the u, v directions changes the potential energy. Let r_{ij0} be the separation between the i-th and j-th atoms in equilibrium. If we express the potential energy in a Taylor series, we have

$$(2)\quad \sum_{\substack{\text{all}\\ \text{pairs}}} V(r_{ij}) = \sum_{\substack{\text{all}\\ \text{pairs}}} \Big\{ V(r_{ij0}) + (u_j - u_i)\frac{\partial V(r_{ij0})}{\partial x} + (v_j - v_i)\frac{\partial V(r_{ij0})}{\partial y} + (u_j - u_i)(v_j - v_i)\frac{\partial^2 V(r_{ij0})}{\partial x \partial y} + \tfrac{1}{2}(u_j - u_i)^2 \frac{\partial^2 V(r_{ij0})}{\partial x^2} + \tfrac{1}{2}(v_j - v_i)^2 \frac{\partial^2 V(r_{ij0})}{\partial y^2} + \cdots \Big\}.$$

Due to small displacements we shall neglect higher order terms and consider only through the second order. Since we can take

$$(3)\quad V(r_{ij0}) = 0 \quad \text{and} \quad \frac{\partial V(r_{ij0})}{\partial x} = \frac{\partial V(r_{ij0})}{\partial y} = 0, \quad \text{then}$$

$$(4)\quad \sum_{\substack{\text{all}\\ \text{pairs}}} V(r_{ij0}) = \sum_{\substack{\text{all}\\ \text{pairs}}} \Big\{ \tfrac{1}{2}(u_j - u_i)^2 V_{xx0} + \tfrac{1}{2}(v_j - v_i)^2 V_{yy0} + (u_j - u_i)(v_j - v_i) V_{xy0} + \cdots \Big\};$$

where

$$(5)\quad V_{xx0} = \frac{\partial^2 V(r_{ij0})}{\partial x^2}; \quad V_{yy0} = \frac{\partial^2 V(r_{ij0})}{\partial y^2}; \quad V_{xy0} = \frac{\partial^2 V(r_{ij0})}{\partial x \partial y}.$$

Differentiation yields

(6) $V_{xyo} = 0$; $V_{xxo} = V_{yyo} = V''(a)$ for nearest neighbors

(7) $V_{xxo} = V_{yyo} = 0$; $V_{xyo} = V''(a\sqrt{2})$ for next nearest neighbors.

Then, that part of the potential energy of the lattice that contains the displacements $u_{l,m}$, $v_{l,m}$ of the l,m-th atom is

$$(8)\quad V_{l,m} = \frac{V''(a)}{2}\left\{(u_{l+1,m}-u_{l,m})^2+(u_{l,m}-u_{l-1,m})^2+(v_{l,m+1}-v_{l,m})^2+(v_{l,m}-v_{l,m-1})^2\right\}$$
$$+\frac{V''(a\sqrt{2})}{2}\left\{(u_{l+1,m+1}-u_{l,m}+v_{l+1,m+1}-v_{l,m})^2+(u_{l,m}-u_{l-1,m+1}+v_{l-1,m+1}-v_{l,m})^2\right.$$
$$\left.+(u_{l,m}-u_{l-1,m-1}+v_{l,m}-v_{l-1,m-1})^2+(u_{l+1,m-1}-u_{l,m}+v_{l,m}-v_{l+1,m-1})^2\right\}.$$

Hence the equations of motion of this atom are

$$(9)\quad M\ddot{u}_{l,m} = -\frac{\partial V_{l,m}}{\partial u_{l,m}} = -\beta\{2u_{l,m}-u_{l-1,m}-u_{l+1,m}\}-\delta\{4u_{l,m}$$
$$-u_{l+1,m+1}-u_{l-1,m+1}-u_{l+1,m-1}-u_{l-1,m-1}$$
$$-v_{l+1,m+1}+v_{l-1,m+1}+v_{l+1,m-1}-v_{l-1,m-1}\}$$

$$(10)\quad M\ddot{v}_{l,m} = -\frac{\partial V_{l,m}}{\partial v_{l,m}} = -\beta\{2v_{l,m}-v_{l-1,m}-v_{l+1,m}\}-\delta\{4v_{l,m}$$
$$-v_{l+1,m+1}-v_{l-1,m+1}-v_{l+1,m-1}-v_{l-1,m-1}$$
$$-u_{l+1,m+1}+u_{l-1,m+1}+u_{l+1,m-1}-u_{l-1,m-1}\}$$

where $\beta = V''(a)$; $\delta = V''(a\sqrt{2})$; M = mass of the atom.

The periodic solutions of the equations of motion are:

(11) $u_{\ell,m} = u' e^{2\pi i(\nu t + \vec{\sigma}\cdot\vec{R})}$ $\qquad v_{\ell,m} = v' e^{2\pi i(\nu t + \vec{\sigma}\cdot\vec{R})}$

where $\vec{\sigma} = \sigma_x \vec{i} + \sigma_y \vec{j} = \sigma_1 \vec{b}_1 + \sigma_2 \vec{b}_2$; $\vec{R} = a(\ell \vec{i} + m\vec{j}) = \ell \vec{d}_1 + m \vec{d}_2$

and ℓ and m go from 1 to N_1 and N_2 respectively, N_1 and N_2 being the total number of atoms in the $\vec{d}_1$ and $\vec{d}_2$ directions. $\vec{i}$ and $\vec{j}$ are unit vectors along the x and y axes. $\vec{R}$ is the position vector, and $\vec{\sigma}$ is the associated wave vector with magnitude $1/\lambda$. Write

(12) $2\pi \vec{\sigma}\cdot\vec{R} = 2\pi a(\ell \sigma_x + m \sigma_y) \equiv \ell \phi_1 + m \phi_2$.

(13) $\vec{d}_1 \equiv a\vec{i}$; $\vec{d}_2 \equiv a\vec{j}$ where a is the lattice constant (Fig. 1). The reciprocal vectors $\vec{b}_1$ and $\vec{b}_2$ are defined by

(14) $\vec{b}_1\cdot\vec{d}_1 = 1$; $\vec{b}_2\cdot\vec{d}_1 = 0$; $\vec{b}_1\cdot\vec{d}_2 = 0$; $\vec{b}_2\cdot\vec{d}_2 = 1$.

Substitution of the periodic solutions into the equations of motion gives:

(15) $u'\left[2\beta(1-\cos\phi_1) + 4\delta(1-\cos\phi_1\cos\phi_2) - 4\pi^2 M\nu^2\right] - 4\delta v' \sin\phi_1 \sin\phi_2 = 0$

$v'\left[2\beta(1-\cos\phi_2) + 4\delta(1-\cos\phi_1\cos\phi_2) - 4\pi^2 M\nu^2\right] - 4\delta u' \sin\phi_1 \sin\phi_2 = 0$

whence

(16) $$\begin{vmatrix} a_1 + 2a_{12} - \gamma & -2b \\ -2b & a_2 + 2a_{12} - \gamma \end{vmatrix}$$

where

$a_i = \beta(1-\cos\phi_i)$

$a_{ij} = \delta(1-\cos\phi_i\cos\phi_j)$

$b = \delta \sin\phi_1 \sin\phi_2$

$\gamma = 2\pi^2 M\nu^2$

Solution of this secular determinant will give the frequency ν in terms of the ϕ's.

The Cubic Lattice.

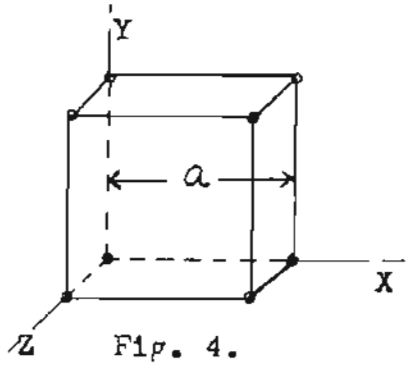

Fig. 4.

The Reciprocal of the Cubic Lattice.

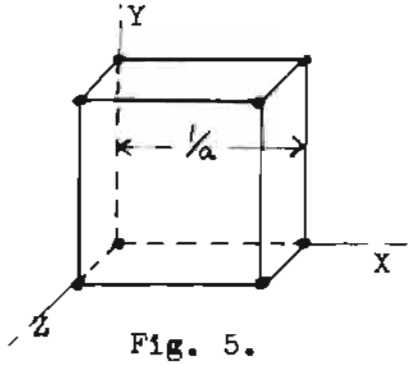

Fig. 5.

The First Brillouin Zone for the Cubic Lattice.

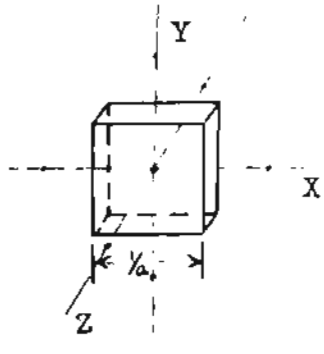

Fig. 6.

THE SIMPLE CUBIC LATTICE

Now consider the simple cubic lattice. The unit cell is shown in Fig. 4 as a cube with lattice points at the eight corners. If a is the lattice spacing the volume in the direct lattice is $V_d = a^3$.

The basis vectors are:

$\vec{d}_1 = a\vec{i}$; $\vec{d}_2 = a\vec{j}$; $\vec{d}_3 = a\vec{k}$; where $\vec{i}$, $\vec{j}$, $\vec{k}$, are unit vectors along the x, y, z axes respectively. The position vector for lattice point (ℓ, m, n) in relation to the point taken as origin is

(17) $\vec{R} = \ell\vec{d}_1 + m\vec{d}_2 + n\vec{d}_3 = a(\ell\vec{i} + m\vec{j} + n\vec{k})$

where ℓ, m and n are integers.

As in the case of the square lattice we shall use the reciprocal lattice of the simple cube. Fig. 5 shows the reciprocal lattice of the direct cubic lattice. It is a cube with the points represented by dots at the cube corners. The magnitude of the reciprocal lattice basis vectors is determined by taking the reciprocal of the magnitude of the direct lattice basis vectors. Then draw this reciprocal lattice vector normal to the plane of the two direct lattice basis vectors not yet used. The other two reciprocal lattice basis vectors may be obtained in like manner. The result will give three orthogonal basis vectors for the reciprocal lattice of the simple cube.

In order to prevent ambiguity in the wave lengths and the frequencies of vibration a zone is formed about the origin in the reciprocal lattice. This zone is bounded by planes which

are perpendicular bisectors of the lines joining the reciprocal lattice sites. The zone, known as the first Brillouin Zone, includes a complete period in every direction of vibration and contains all allowable frequencies. From Fig. 6 it may be seen that this zone is a simple cube.

Giving an atom displacements u, v, and w in the x, y, and z directions, respectively, will set up a potential energy. This potential energy can be taken as zero when the atom is in its equilibrium position. Only the nearest and next nearest neighbors will be considered.

Using the Taylor expansion of the potential energy function in the same way as was done with the square lattice the potential energy may be expressed as

(18)
$$\sum_{\substack{\text{all}\\ \text{pairs}}} V(r_{ij}) = \sum_{\substack{\text{all}\\ \text{pairs}}} \Big\{ V(r_{ij0}) + (u_j - u_i) V_{x,0} + (v_j - v_i) V_{y,0} + (\omega_j - \omega_i) V_{z,0} + \tfrac{1}{2}(u_j - u_i)^2 V_{xx,0} + \tfrac{1}{2}(v_j - v_i)^2 V_{yy,0} + \tfrac{1}{2}(\omega_j - \omega_i)^2 V_{zz,0} + (u_j - u_i)(v_j - v_i) V_{xy,0} + (v_j - v_i)(\omega_j - \omega_i) V_{yz,0} + (\omega_j - \omega_i)(u_j - u_i) V_{zx,0} + \cdots \Big\}$$

For nearest neighbors $i = \ell, m, n$ and $j = \ell+1, m, n$.

$V(r_o) = V(a)$.

(19)
$$V_{xx,0} = \left[\frac{\partial^2}{\partial x^2} \left(V\sqrt{(x+a)^2 + y^2 + z^2} \right) \right]_{\substack{x=0\\ y=0\\ z=0}} = V''(a)$$

$$V_{yy,0} = V_{zz,0} = \tfrac{1}{a} V'(a); \quad V_{xy,0} = V_{yz,0} = V_{zx,0} = 0 .$$

For next nearest neighbors $i = \ell, m, n$ and $j = \ell+1, m+1, n$. $V(r_0) = V(a\sqrt{2})$.

(20) $V_{x x,0} = \left[\frac{\partial^2}{\partial x^2}\left(V\sqrt{(x+a)^2+(y+a)^2+z^2}\right)\right]_{\substack{x=0\\y=0\\z=0}} = -\frac{1}{2\sqrt{2}\,a} V'(a\sqrt{2}) + \frac{1}{2} V''(a\sqrt{2})$.

$$V_{x x,0} = V_{y y,0}\ ;\ V_{z z,0} = \frac{1}{\sqrt{2}\,a} V'(a\sqrt{2})$$

$$V_{x y,0} = \frac{1}{2\sqrt{2}\,a} V'(a\sqrt{2}) + \frac{1}{2} V''(a\sqrt{2}).\quad V_{y z,0} = V_{z x,0} = 0.$$

where $V' \ll V''$.

Considering only the nearest and next nearest neighbors, writing $V''(a) = \beta$ and $\frac{1}{2} V''(a\sqrt{2}) = \delta$, and using

(21) $\Sigma(u_j - u_i) = \Sigma(v_j - v_i) = \Sigma(w_j - w_i) = 0$; then

(22) $V_{\ell,m,n} = \frac{1}{2}\beta\Big[(u_{\ell+1,m,n} - u_{\ell,m,n})^2 + (u_{\ell,m,n} - u_{\ell-1,m,n})^2$
$(v_{\ell,m+1,n} - v_{\ell,m,n})^2 + (v_{\ell,m,n} - v_{\ell,m-1,n})^2$
$(w_{\ell,m,n+1} - w_{\ell,m,n})^2 + (w_{\ell,m,n} - w_{\ell,m,n-1})^2\Big]$
$+ \frac{1}{2}\delta\Big[(u_{\ell+1,m+1,n} - u_{\ell,m,n} + v_{\ell+1,m+1,n} - v_{\ell,m,n})^2$
$+(v_{\ell,m+1,n-1} - v_{\ell,m,n} + w_{\ell,m,n} - w_{\ell,m+1,n-1})^2$
$+(u_{\ell,m,n} - u_{\ell-1,m+1,n} + v_{\ell-1,m+1,n} - v_{\ell,m,n})^2$
$+(v_{\ell,m+1,n+1} - v_{\ell,m,n} + w_{\ell,m+1,n+1} - w_{\ell,m,n})^2$
$+(u_{\ell+1,m,n+1} - u_{\ell,m,n} + w_{\ell+1,m,n+1} - w_{\ell,m,n})^2$
$+(u_{\ell+1,m,n-1} - u_{\ell,m,n} + w_{\ell,m,n} - w_{\ell+1,m,n-1})^2$
$+(u_{\ell,m,n} - u_{\ell-1,m,n-1} + w_{\ell,m,n} - w_{\ell-1,m,n-1})^2$
$+(u_{\ell,m,n} - u_{\ell-1,m,n+1} + w_{\ell-1,m,n+1} - w_{\ell,m,n})^2$

$$+(u_{\ell+1,m-1,n} - u_{\ell,m,n} + v_{\ell,m,n} - v_{\ell+1,m-1,n})^2$$

$$+(v_{\ell,m,n} - v_{\ell,m-1,n-1} + w_{\ell,m,n} - w_{\ell,m-1,n-1})^2$$

$$+(u_{\ell,m,n} - u_{\ell-1,m-1,n} + v_{\ell,m,n} - v_{\ell-1,m-1,n})^2$$

$$+(v_{\ell,m,n} - v_{\ell,m-1,n+1} + w_{\ell,m-1,n+1} - w_{\ell,m,n})^2\Big] .$$

Taking the negative derivative of the potential energy with respect to the displacement gives the force which may be used to obtain the equation of motion

(23) $$M\ddot{u}_{\ell,m,n} = -\frac{\partial V_{\ell,m,n}}{\partial u_{\ell,m,n}} = -\beta\left[2u_{\ell,m,n} - u_{\ell+1,m,n} - u_{\ell-1,m,n}\right]$$

$$-\delta\Big[8u_{\ell,m,n} - u_{\ell+1,m+1,n} - u_{\ell-1,m+1,n} - u_{\ell+1,m,n+1}$$

$$- u_{\ell+1,m,n-1} - u_{\ell-1,m,n-1} - u_{\ell-1,m,n+1}$$

$$- u_{\ell+1,m-1,n} - u_{\ell-1,m-1,n} - v_{\ell+1,m+1,n}$$

$$+ v_{\ell-1,m+1,n} + v_{\ell+1,m-1,n} - v_{\ell-1,m-1,n}$$

$$- w_{\ell+1,m,n+1} + w_{\ell+1,m,n-1} - w_{\ell-1,m,n-1}$$

$$+ w_{\ell-1,m,n+1}\Big] \quad \text{with similar equations}$$

for $\ddot{v}_{\ell,m,n}$ and $\ddot{w}_{\ell,m,n}$.

For a periodic solution of the equations of motion let

(24) $$u_{\ell,m,n} = u' e^{i(2\pi\nu t + \ell\phi_1 + m\phi_2 + n\phi_3)} .$$

$$v_{\ell,m,n} = v' e^{i(2\pi\nu t + \ell\phi_1 + m\phi_2 + n\phi_3)} .$$

$$w_{\ell,m,n} = w' e^{i(2\pi\nu t + \ell\phi_1 + m\phi_2 + n\phi_3)} .$$

Substitution of this solution in the equations of motion yields

$$(25)\quad 0 = u'\left[\beta(1-\cos\phi_1) + 2\delta(2-\cos\phi_1\cos\phi_2 - \cos\phi_3\cos\phi_4 - 2\pi^2\nu^2 M)\right] + 2v'\delta\sin\phi_1\sin\phi_2 + 2w'\delta\sin\phi_3\sin\phi_1 .$$

$$0 = v'\left[\beta(1-\cos\phi_2) + 2\delta(2-\cos\phi_2\cos\phi_3 - \cos\phi_1\cos\phi_2 - 2\pi^2\nu^2 M)\right] + 2w'\delta\sin\phi_2\sin\phi_3 + 2u'\delta\sin\phi_1\sin\phi_2 .$$

$$0 = w'\left[\beta(1-\cos\phi_3) + 2\delta(2-\cos\phi_1\cos\phi_4 - \cos\phi_2\cos\phi_3 - 2\pi^2\nu^2 M)\right] + 2u'\delta\sin\phi_3\sin\phi_1 + 2v'\delta\sin\phi_2\sin\phi_3 .$$

Hence

$$(26)\quad 0 = \begin{vmatrix} a_1\beta + 2a_{23}\delta - y & 2b_{12}\delta & 2b_{31}\delta \\ 2b_{12}\delta & a_2\beta + 2a_{31}\delta - y & 2b_{23}\delta \\ 2b_{31}\delta & 2b_{23}\delta & a_3\beta + 2a_{12}\delta - y \end{vmatrix}$$

where $a_i = 1 - \cos\phi_i$

$a_{ij} = 2 - \cos\phi_j\cos\phi_k - \cos\phi_k\cos\phi_i$

$b_{ij} = 2\sin\phi_i\sin\phi_j$

$y = 4\pi^2\nu^2 M$

This secular determinant could now be solved for ν (the frequency) in terms of the ϕ's.

BODY-CENTERED CUBIC LATTICE

THE GEOMETRY OF THE BODY-CENTERED CUBIC LATTICE

This lattice cell consists of a cube with an atom at each corner and one at the center of the cube. In the discussion only the nearest and the next nearest neighbors will be considered about the atom at the center of a lattice cell taken as the origin. There will be eight nearest neighbors, the atoms at the corners of the lattice cell; there will be six next nearest neighbors, the atoms at the centers of the adjacent cells.

The position vector is

(12) $$\vec{R} = x\vec{i} + y\vec{j} + z\vec{k} = l_1\vec{d}_1 + l_2\vec{d}_2 + l_3\vec{d}_3$$

where l_1, l_2, l_3 are integers from 1 to N_1, N_2, N_3 respectively and $\vec{d}_1 = a/2\ (\vec{i} + \vec{j} - \vec{k})$ $\vec{d}_2 = a/2\ (-\vec{i} + \vec{j} + \vec{k})$; $\vec{d}_3 = a/2\ (\vec{i} - \vec{j} + \vec{k})$ are the basis vectors. The volume of the unit cell in direct space is $V_d = \vec{d}_1 \cdot \vec{d}_2 \cdot \vec{d}_3 = a^3/2$. Also $x = l\frac{a}{2}$, $y = m\frac{a}{2}$, $z = n\frac{a}{2}$, where a is the lattice constant, and l, m, n are integers.

The Body Centered Cubic Lattice.

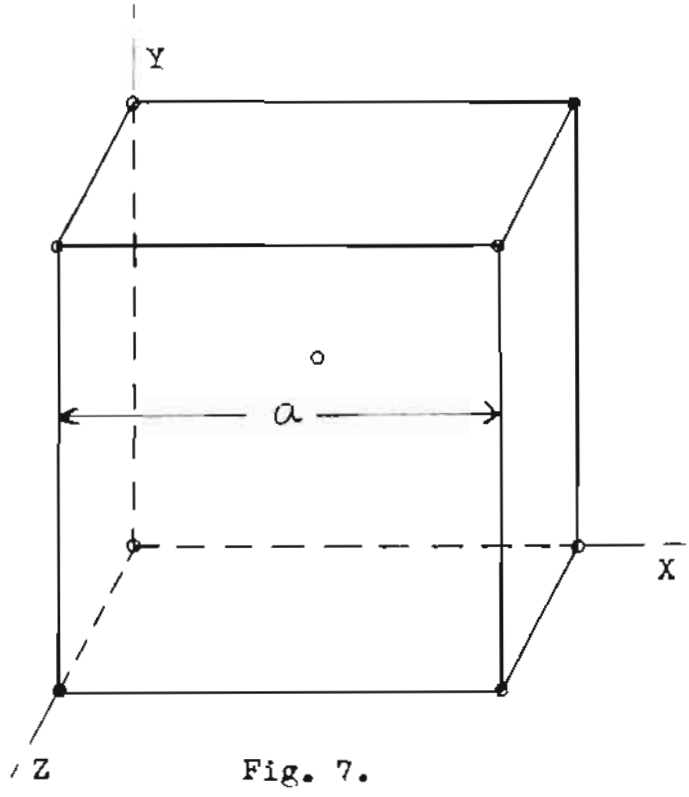

Fig. 7.

The Reciprocal of the Body-Centered Cubic Lattice.

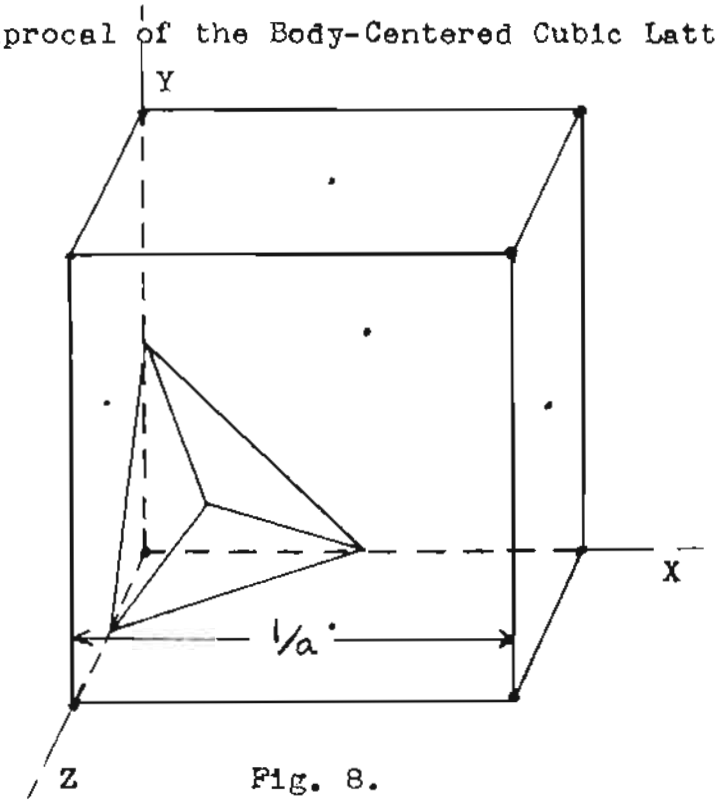

Fig. 8.

The First Brillouin Zone for
the Body-Centered Cubic Lattice

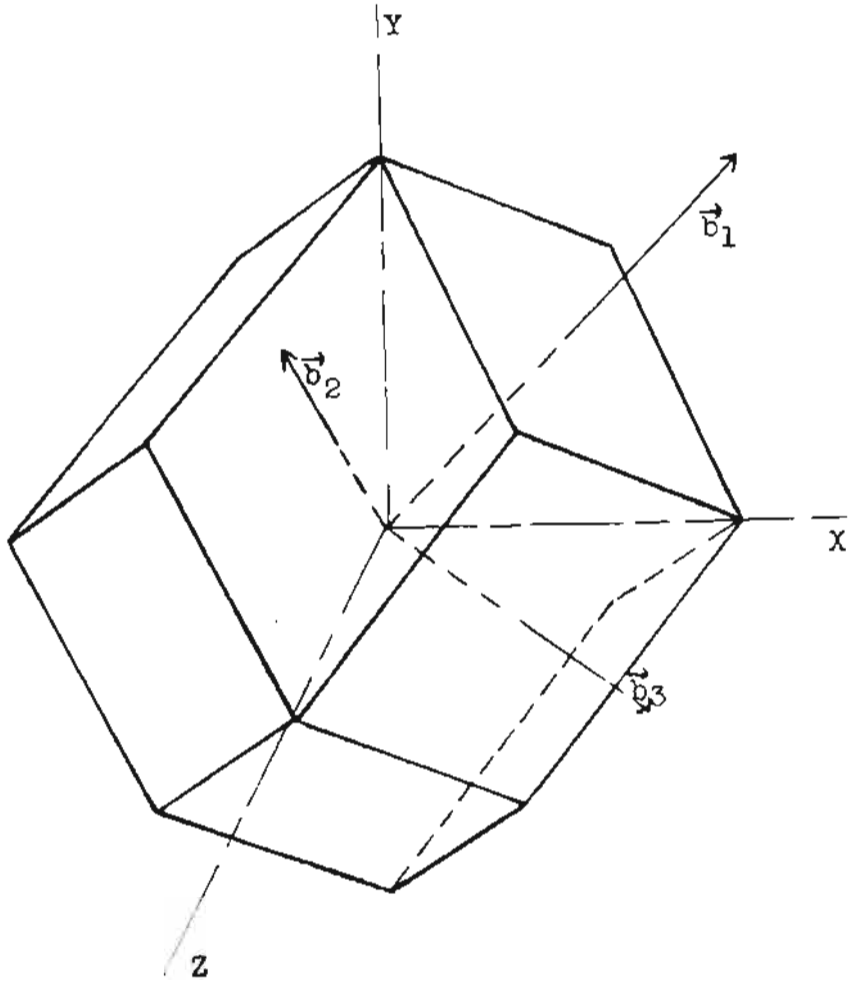

Fig. 9.

THE RECIPROCAL LATTICE

The reciprocal lattice results from taking the reciprocal of the basis vectors, as was described for the simple cubic case, and obtaining a new lattice space. This is shown in Fig. 8 to be a face-centered cubic lattice. Also shown in Fig. 8 is one octant of the first Brillouin Zone, which is a pyramid extending out into the center of the reciprocal lattice diagram. The method for obtaining this zone is described in the simple cubic case. The wave vector will be

(28) $\vec{\sigma} = \sigma_x \vec{\imath} + \sigma_y \vec{\jmath} + \sigma_z \vec{k} = \sigma_1 \vec{b}_1 + \sigma_2 \vec{b}_2 + \sigma_3 \vec{b}_3$

where $\sigma_i = m_i/N_i$; $m_i = 1$ to N_i, $i = 1,2,3$, and N_i is the number of atoms along the $\vec{d}_i$ direction. The total number of atoms $N_1 \times N_2 \times N_3$ in the crystal equals the number of σ points in the reciprocal unit cell. The vectors $\vec{b}_i$ are reciprocal to the $\vec{d}_i$, and are given by

(29) $\vec{b}_1 = \frac{1}{a}(\vec{\imath} + \vec{\jmath})$; $\vec{b}_2 = \frac{1}{a}(\vec{\jmath} + \vec{k})$; $\vec{b}_3 = \frac{1}{a}(\vec{k} + \vec{\imath})$.

Also

(30) $\sigma_x = \sigma_1(\vec{\imath} \cdot \vec{b}_1) + \sigma_2(\vec{\jmath} \cdot \vec{b}_2) + \sigma_3(\vec{\imath} \cdot \vec{b}_3) = \frac{1}{a}\left(\frac{m_3}{N_3} + \frac{m_1}{N_1}\right)$

$\sigma_y = \sigma_1(\vec{\jmath} \cdot \vec{b}_1) + \sigma_2(\vec{\jmath} \cdot \vec{b}_2) + \sigma_3(\vec{\jmath} \cdot \vec{b}_3) = \frac{1}{a}\left(\frac{m_2}{N_2} + \frac{m_3}{N_3}\right)$

$\sigma_z = \sigma_1(\vec{k} \cdot \vec{b}_1) + \sigma_2(\vec{k} \cdot \vec{b}_2) + \sigma_3(\vec{k} \cdot \vec{b}_3) = \frac{1}{a}\left(\frac{m_2}{N_2} + \frac{m_1}{N_1}\right)$

and

(31) $2\pi \vec{\sigma} \cdot \vec{R} = \pi a(l\sigma_x + m\sigma_y + n\sigma_z) = l\phi_1 + m\phi_2 + n\phi_3$.

Hence,

$$(32)\qquad \phi_1 = \pi\left(\frac{m_3}{N_3} + \frac{m_1}{N_1}\right) = \pi\left(\sigma_3 + \sigma_1\right)$$

$$\phi_2 = \pi\left(\frac{m_1}{N_1} + \frac{m_2}{N_2}\right) = \pi\left(\sigma_1 - \sigma_2\right)$$

$$\phi_3 = \pi\left(\frac{m_2}{N_2} + \frac{m_3}{N_3}\right) = \pi\left(\sigma_2 + \sigma_3\right) .$$

The volume of the reciprocal unit cell, $V_b = 2/a^3$ = volume of the first Brillouin Zone. Fig. 9 shows the resultant zone (Brillouin Zone) to be a twelve sided figure bounded by diamond shaped parallelograms. This is the first Brillouin Zone for the body-centered cubic direct lattice.

THE POTENTIAL ENERGY AND FORCE CONSTANTS

Notation: Atom i has displacements u_i in x-direction, v_i in y-direction, w_i in z-direction. Atoms i and j have potential energy $V(r_{ij})$, where r_{ij} is the separation. Subscript o refers to equilibrium position of the atoms. Then the potential energy of the lattice is

(33) $$V = \sum_{\substack{\text{all}\\ \text{pairs}}} V(r_{ij}) = \sum_{\substack{\text{all}\\ \text{pairs}}} \Big[V(r_{ij,0}) + (u_j - u_i) V_{x,0} + (v_j - v_i) V_{y,0}$$
$$+ (w_j - w_i) V_{z,0} + \tfrac{1}{2}(u_j - u_i)^2 V_{xx,0} + \tfrac{1}{2}(v_j - v_i)^2 V_{yy,0}$$
$$+ \tfrac{1}{2}(w_j - w_i)^2 V_{zz,0} + (u_j - u_i)(v_j - v_i) V_{xy,0}$$
$$+ (v_j - v_i)(w_j - w_i) V_{yz,0} + (w_j - w_i)(u_j - u_i) V_{zx,0} + \text{higher order terms} \Big].$$

For an infinite lattice

(34) $$\sum_{\substack{\text{all}\\ \text{pairs}}} (u_j - u_i) = \sum_{\substack{\text{all}\\ \text{pairs}}} (v_j - v_i) = \sum_{\substack{\text{all}\\ \text{pairs}}} (w_j - w_i) = 0,$$ and we can take

$$\Sigma V(r_{ij,0}) = 0.$$

For nearest neighbors taking $i = (l, m, n)$, then $j = (l \pm \tfrac{1}{2}, m \pm \tfrac{1}{2}, n \pm \tfrac{1}{2})$. And

(35) $$V_{xx,0} = \left[\frac{\partial^2}{\partial x^2} \left(V\sqrt{(x \pm a/2)^2 + (y \pm a/2)^2 + (z \pm a/2)^2} \right) \right]_{\substack{x=0\\ y=0\\ z=0}} = \tfrac{1}{3} V''(\tfrac{a}{2}\sqrt{3})$$
$$+ \tfrac{1}{2\sqrt{3}} V'(\tfrac{a}{2}\sqrt{3}) - \tfrac{1}{3\frac{a}{2}\sqrt{3}} V'(\tfrac{a}{2}\sqrt{3}) = V_{yy,0} = V_{zz,0}.$$

$$V_{xy,0} = V_{yz,0} = V_{zx,0} = \tfrac{1}{3} V''(\tfrac{a}{2}\sqrt{3}) - \frac{1}{3\frac{a}{2}\sqrt{3}} V'(\tfrac{a}{2}\sqrt{3}).$$

For next nearest neighbors $i = (\ell, m, n)$ and $j = (\ell \pm 1, m, n)$, $(\ell, m \pm 1, n)$, or $(\ell, m, n \pm 1)$. Differentiation yields

$$(36)\quad V_{xx,o} = V_{yy,o} = V_{zz,o} = \left[\frac{\partial^2}{\partial x^2}\left(V\sqrt{(x \pm a)^2 + y^2 + z^2}\right)\right]_{\substack{x=0\\y=0\\z=0}} = V''(a)$$

$$V_{xy,o} = V_{yz,o} = V_{zx,o} = 0.$$

Denote $1/3\ V''(a\sqrt{3})$ by β, $V''(a)$ by δ, assume $1/a\ V' \ll V''$, and neglect the higher-order terms.

Then the potential energy of the lattice involving $u_{l,m,n}$, $v_{l,m,n}$, $w_{l,m,n}$ is:

$$\begin{aligned}(37)\quad V_{l,m,n} = {} & 1/6\ V''(a\sqrt{3})\Big[(u_{l+1,m+1,n+1} - u_{l,m,n})^2 + (v_{l+1,m+1,n+1} - v_{l,m,n})^2 \\ & + (w_{l+1,m+1,n+1} - w_{l,m,n})^2 + (u_{l+1,m+1,n-1} - u_{l,m,n})^2 \\ & + (v_{l+1,m+1,n-1} - v_{l,m,n})^2 + (w_{l,m,n} - w_{l-1,m+1,n-1})^2 \\ & + (u_{l,m,n} - u_{l-1,m+1,n-1})^2 + (v_{l-1,m+1,n-1} - v_{l,m,n})^2 \\ & + (w_{l,m,n} - w_{l-1,m+1,n-1})^2 + (u_{l,m,n} - u_{l-1,m+1,n+1})^2 \\ & + (v_{l-1,m+1,n+1} - v_{l,m,n})^2 + (w_{l-1,m+1,n+1} - w_{l,m,n})^2 \\ & + (u_{l+1,m-1,n+1} - u_{l,m,n})^2 + (v_{l,m,n} - v_{l+1,m-1,n+1})^2 \\ & + (w_{l+1,m-1,n+1} - w_{l,m,n})^2 + (u_{l+1,m-1,n-1} - u_{l,m,n})^2 \\ & + (v_{l,m,n} - v_{l+1,m-1,n-1})^2 + (w_{l,m,n} - w_{l+1,m-1,n-1})^2 \\ & + (u_{l,m,n} - u_{l-1,m-1,n-1})^2 + (v_{l,m,n} - v_{l-1,m-1,n-1})^2 \\ & + (w_{l,m,n} - w_{l-1,m-1,n-1})^2 + (u_{l,m,n} - u_{l-1,m-1,n+1})^2 \\ & + (v_{l,m,n} - v_{l-1,m-1,n+1})^2 + (w_{l-1,m-1,n+1} - w_{l,m,n})^2\Big]\end{aligned}$$

$$
\begin{aligned}
+ 2/3\, V''(\tfrac{2}{\ell}\sqrt{3}) \Big[& (u_{\ell+1,m+1,n+1} - u_{\ell,m,n})(v_{\ell+1,m+1,n+1} - v_{\ell,m,n}) \\
& + (u_{\ell+1,m+1,n-1} - u_{\ell,m,n})(v_{\ell+1,m+1,n-1} - v_{\ell,m,n}) \\
& + (u_{\ell,m,n} - u_{\ell-1,m+1,n-1})(v_{\ell-1,m+1,n-1} - v_{\ell,m,n}) \\
& + (u_{\ell,m,n} - u_{\ell-1,m+1,n+1})(v_{\ell-1,m+1,n+1} - v_{\ell,m,n}) \\
& + (u_{\ell+1,m-1,n+1} - u_{\ell,m,n})(v_{\ell,m,n} - v_{\ell+1,m-1,n+1}) \\
& + (u_{\ell+1,m-1,n-1} - u_{\ell,m,n})(v_{\ell,m,n} - v_{\ell+1,m-1,n-1}) \\
& + (u_{\ell,m,n} - u_{\ell-1,m-1,n-1})(v_{\ell,m,n} - v_{\ell-1,m-1,n-1}) \\
& + (u_{\ell,m,n} - u_{\ell-1,m-1,n+1})(v_{\ell,m,n} - v_{\ell-1,m-1,n+1}) \\
& + (v_{\ell+1,m+1,n+1} - v_{\ell,m,n})(w_{\ell+1,m+1,n+1} - w_{\ell,m,n}) \\
& + (v_{\ell+1,m+1,n-1} - v_{\ell,m,n})(w_{\ell,m,n} - w_{\ell+1,m+1,n-1}) \\
& + (v_{\ell-1,m+1,n-1} - v_{\ell,m,n})(w_{\ell,m,n} - w_{\ell-1,m+1,n-1}) \\
& + (v_{\ell-1,m+1,n+1} - v_{\ell,m,n})(w_{\ell-1,m+1,n+1} - w_{\ell,m,n}) \\
& + (v_{\ell,m,n} - v_{\ell+1,m-1,n+1})(w_{\ell+1,m-1,n+1} - w_{\ell,m,n}) \\
& + (v_{\ell,m,n} - v_{\ell+1,m-1,n-1})(w_{\ell,m,n} - w_{\ell+1,m-1,n-1}) \\
& + (v_{\ell,m,n} - v_{\ell-1,m-1,n-1})(w_{\ell,m,n} - w_{\ell-1,m-1,n-1}) \\
& + (v_{\ell,m,n} - v_{\ell-1,m-1,n+1})(w_{\ell-1,m-1,n+1} - w_{\ell,m,n})
\end{aligned}
$$

$$+ (w_{\ell+1,m+1,n+1} - w_{\ell,m,n})(u_{\ell+1,m+1,n+1} - u_{\ell,m,n})$$

$$+ (w_{\ell,m,n} - w_{\ell+1,m+1,n-1})(u_{\ell+1,m+1,n-1} - u_{\ell,m,n})$$

$$+ (w_{\ell,m,n} - w_{\ell-1,m+1,n-1})(u_{\ell,m,n} - u_{\ell-1,m+1,n-1})$$

$$+ (w_{\ell-1,m+1,n+1} - w_{\ell,m,n})(u_{\ell,m,n} - u_{\ell-1,m+1,n+1})$$

$$+ (w_{\ell+1,m-1,n+1} - w_{\ell,m,n})(u_{\ell+1,m-1,n+1} - u_{\ell,m,n})$$

$$+ (w_{\ell,m,n} - w_{\ell+1,m-1,n-1})(u_{\ell+1,m-1,n-1} - u_{\ell,m,n})$$

$$+ (w_{\ell,m,n} - w_{\ell-1,m-1,n-1})(u_{\ell,m,n} - u_{\ell-1,m-1,n-1})$$

$$+ (w_{\ell-1,m-1,n+1} - w_{\ell,m,n})(u_{\ell,m,n} - u_{\ell-1,m-1,n+1})\Big]$$

$$+ \tfrac{1}{2} V''(a)\Big[(u_{\ell+2,m,n} - u_{\ell,m,n})^2 + (v_{\ell,m+2,n} - v_{\ell,m,n})^2$$

$$+ (u_{\ell,m,n} - u_{\ell-2,m,n})^2 + (v_{\ell,m,n} - v_{\ell,m-2,n})^2$$

$$+ (w_{\ell,m,n+2} - w_{\ell,m,n})^2 + (w_{\ell,m,n} - w_{\ell,m,n-2})^2\Big] .$$

The equations of motion are

$$(38)\quad M\ddot{u}_{\ell,m,n} = -\frac{\partial V_{\ell,m,n}}{\partial u_{\ell,m,n}} = -\tfrac{1}{3} V'(\tfrac{a}{2}\sqrt{3})\Big[8u_{\ell,m,n} - u_{\ell+1,m+1,n+1}$$

$$- u_{\ell-1,m-1,n-1} - u_{\ell+1,m+1,n-1} - u_{\ell-1,m-1,n+1} - u_{\ell-1,m+1,n-1}$$

$$- u_{\ell+1,m-1,n+1} - u_{\ell-1,m+1,n+1} - u_{\ell+1,m-1,n-1} - v_{\ell+1,m+1,n+1}$$

$$- v_{\ell-1,m-1,n-1} - v_{\ell+1,m+1,n-1} - v_{\ell-1,m-1,n+1} + v_{\ell-1,m+1,n-1}$$

$$+ v_{\ell+1,m-1,n+1} + v_{\ell-1,m+1,n+1} + v_{\ell+1,m-1,n-1} - w_{\ell+1,m+1,n+1}$$

$$- w_{\ell-1,m-1,n-1} + w_{\ell+1,m+1,n-1} + w_{\ell-1,m-1,n+1} - w_{\ell-1,m+1,n-1}$$

$$- w_{\ell+1,m-1,n+1} + w_{\ell-1,m+1,n+1} + w_{\ell+1,m-1,n-1}\Big]$$

$$- V''(a)\left[2u_{\ell,m,n} - u_{\ell+2,m,n} - u_{\ell-2,m,n}\right].$$

plus similar equations for $v_{\ell,m,n}$ and $w_{\ell,m,n}$.

The periodic solutions of the equations of motion are:

$$(39)\quad u_{\ell,m,n} = u' e^{i\{2\pi\nu t + \ell\phi_1 + m\phi_2 + n\phi_3\}}$$
$$v_{\ell,m,n} = v' e^{i\{2\pi\nu t + \ell\phi_1 + m\phi_2 + n\phi_3\}}$$
$$w_{\ell,m,n} = w' e^{i\{2\pi\nu t + \ell\phi_1 + m\phi_2 + n\phi_3\}}$$

Substituting the periodic solutions in the equations of motion yields

$$(40)\quad 0 = -4\pi^2\nu^2 M u' + \gamma\beta\left[u'(1 - C_1C_2C_3) + v'(S_1S_2C_3) + w'(S_3S_1C_2)\right] + 4\delta S_1^2 u'.$$
$$0 = -4\pi^2\nu^2 M v' + 8\beta\left[v'(1 - C_1C_2C_3) + w'(S_2S_3C_1) + u'(S_1S_2C_3)\right] + 4\delta S_2^2 v'.$$
$$0 = -4\pi^2\nu^2 M w' + 8\beta\left[w'(1 - C_1C_2C_3) + u'(S_3S_1C_2) + v'(S_2S_3C_1)\right] + 4\delta S_3^2 w'.$$

Hence

$$(41)\quad 0 = -\left(\frac{y}{\pi}\right)^2 u' + 2\alpha\left[u'(1 - C_1C_2C_3) + v'(S_1S_2C_3) + w'(S_3S_1C_2)\right] + \gamma u' S_1^2.$$
$$0 = -\left(\frac{y}{\pi}\right)^2 v' + 2\alpha\left[v'(1 - C_1C_2C_3) + w'(S_2S_3C_1) + u'(S_1S_2C_3)\right] + \gamma v' S_2^2.$$
$$0 = -\left(\frac{y}{\pi}\right)^2 w' + 2\alpha\left[w'(1 - C_1C_2C_3) + u'(S_3S_1C_2) + v'(S_2S_3C_1)\right] + \gamma w' S_3^2.$$

where $C_i = \cos\phi_i$, $S_i = \sin\phi_i$, $i = 1, 2, 3$,

$$\alpha = \frac{\beta}{M}\left(\frac{h}{2\pi^2 kT}\right)^2;\quad \gamma = \frac{\delta}{M}\left(\frac{h}{2\pi^2 kT}\right)^2;\quad y = \frac{h\nu}{2kT}$$

THE SECULAR DETERMINANT

From these equations we obtain

$$(42)\qquad \begin{vmatrix} b_1 - b_0 - (\gamma/\pi)^2 & a_{12} & a_{31} \\ a_{12} & b_2 - b_0 - (\gamma/\pi)^2 & a_{23} \\ a_{31} & a_{23} & b_3 - b_0 - (\gamma/\pi)^2 \end{vmatrix} \equiv 0$$

where

$$\begin{cases} a_{ij} = 2\alpha \cos\phi_k \sin\phi_i \sin\phi_j \\ b_0 = 2\alpha \cos^2\phi_i \cos^2\phi_j \cos^2\phi_k \\ b_i = 2\alpha + \gamma \sin^2\phi_i \end{cases}$$

Expanding the determinant yields

(43) $$0 \equiv -\left(\frac{y}{\pi}\right)^6 + F\left(\frac{y}{\pi}\right)^4 - G\left(\frac{y}{\pi}\right)^2 + H \quad \text{where}$$

(44) $$F = b_1 + b_2 + b_3 - 3b_0 = 6\alpha\left[1-(123)\right] + \gamma\left[3-(1^2)\right]$$

$$G = (b_1-b_0)(b_2-b_0) + (b_2-b_0)(b_3-b_0) + (b_3-b_0)(b_1-b_0) + a_{12}^2 + a_{23}^2 + a_{31}^2$$

$$= 4\alpha^2\left[3 - 6(123) + 6(123)^2 - 2(1^2 2^2) + (1^2)\right]$$

$$+ 4\alpha\gamma\left[3 - 3(123) + (123)(1^2) - (1^2)\right] + \gamma^2\left[3 + (1^2 2^2) - 2(1^2)\right]$$

$$H = (b_1-b_0)(b_2-b_0)(b_3-b_0) + 2a_{12}a_{23}a_{31} - a_{12}^2(b_3-b_0) - a_{23}^2(b_1-b_0) - a_{31}^2(b_2-b_0)$$

$$= 8\alpha^3\left[1 - (123) - (123)(1^2) - (1^2) + 2(1^2 2^2)\right]$$

$$+ 4\alpha^2\gamma\left[3 + 6(123) - 2(123)(1^2) - 2(1^2) + 2(1^2 2^2) - (1^4 2^2) + (1^4)\right]$$

$$+ 2\alpha\gamma^2\left[3 + 3(123) - 3(1^2)(123) + (123)(1^2 2^2) - 2(1^2) + (1^2 2^2)\right]$$

$$+ \gamma^3\left[1 - (123)^2 - (1^2) + (1^2 2^2)\right].$$

and

(45) $$(123) = c_1 c_2 c_3 \; ; \; (1^2) = c_1^2 + c_2^2 + c_3^2 \; ;$$

$$(1^2 2^2) = c_1^2 c_2^2 + c_2^2 c_3^2 + c_3^2 c_1^2 \; ; \; (1^4) = c_1^4 + c_2^4 + c_3^4 \; ;$$

$$(1^4 2^2) = c_1^4 c_2^2 + c_2^4 c_3^2 + c_3^4 c_1^2 + c_1^2 c_2^4 + c_2^2 c_3^4 + c_3^2 c_1^4 \; ;$$

etc.

THE ENERGY

The secular determinant is now to be solved for ν (the frequency) in terms of the ϕ's. The variables are now changed from the ϕ's to the σ_x, σ_y, σ_z. Since the density of the σ points $= N_1N_2N_3/a^3$, the lattice energy may be expressed as

$$(46)\quad E = \sum_{\substack{\sigma \text{ pts.} \\ \text{in Br. zone}}} \left[\sum_{i=1}^{3} h\nu_i \left(\frac{1}{e^{h\nu_i/kT} - 1} + \frac{1}{2} \right) \right]$$

$$= \iiint_{\substack{\text{Br.} \\ \text{zone}}} \left[\sum_{i=1}^{3} h\nu_i \left(\frac{1}{e^{h\nu_i/kT} - 1} + \frac{1}{2} \right) \right] \frac{a^3}{2} N_1 N_2 N_3 \, d\sigma_x d\sigma_y d\sigma_z$$

The Brillouin Zone limits of σ_x, σ_y, σ_z are $\pm 1/a$.

The energy is

$$(47)\quad E = \frac{N}{2\pi^3} \iiint_{\substack{\text{Br.} \\ \text{zone}}} \left[\frac{h\nu_1}{e^{h\nu_1/kT} - 1} + \frac{h\nu_1}{2} + \frac{h\nu_2}{e^{h\nu_2/kT} - 1} + \frac{h\nu_2}{2} + \frac{h\nu_3}{e^{h\nu_3/kT} - 1} + \frac{h\nu_3}{2} \right] d\phi_1 d\phi_2 d\phi_3$$

Let $y_i = \frac{h\nu_i}{2kT}$. Then, since

$$(48)\quad \frac{2}{e^{2y_i} - 1} + 1 = \frac{2 + e^{2y_i} - 1}{e^{2y_i} - 1} = \frac{e^{2y_i} + 1}{e^{2y_i} - 1} = \frac{e^{y_i} + e^{-y_i}}{e^{y_i} - e^{-y_i}} = \coth y_i$$

$$(49)\quad \frac{2\pi^3 E}{NkT} = \iiint_{\substack{\text{Br.} \\ \text{zone}}} \left[\sum_{i=1}^{3} y_i \coth y_i \right] d\phi_1 d\phi_2 d\phi_3 .$$

Consider the function

(50) $$P = \tfrac{1}{2}\iiint_{\substack{\text{Br.}\\ \text{zone}}} \ln\left(\frac{\sinh y_1}{y_1}\,\frac{\sinh y_2}{y_2}\,\frac{\sinh y_3}{y_3}\right) d\phi_1 d\phi_2 d\phi_3$$

$$= \tfrac{1}{2}\iiint_{\substack{\text{Br.}\\ \text{zone}}} \ln\left[\prod_{i=1}^{3}\frac{\sinh y_i}{y_i}\right] d\phi_1 d\phi_2 d\phi_3$$

$$= \tfrac{1}{2}\iiint_{\substack{\text{Br.}\\ \text{zone}}} \sum_{i=1}^{3} \ln\frac{\sinh y_i}{y_i}\, d\phi_1 d\phi_2 d\phi_3 .$$ Then

(51) $$\lim_{T\to\infty} P = 0 \qquad \lim_{T\to\infty} \frac{E}{T} = 3Nk .$$

(52) Since $d\left(\ln \tfrac{1}{T}\right) = -\frac{dT}{T}$, $\frac{dP}{dT} = -\frac{1}{T}\frac{dP}{d(\ln 1/T)}$,

$$-T\frac{dP}{dT} = \frac{dP}{d(\ln 1/T)}$$, therefore

(53) $$-T\frac{dP}{dT} = \tfrac{1}{2}\iiint_{\substack{\text{Br.}\\ \text{zone}}} \left[\sum_{i=1}^{3} \frac{d\ln\frac{\sinh y_i}{y_i}}{dy_i}\,\frac{dy_i}{d\ln y_i}\right] d\phi_1 d\phi_2 d\phi_3$$

$$= \tfrac{1}{2}\iiint_{\substack{\text{Br.}\\ \text{zone}}} \left[\sum_{i=1}^{3} y_i \coth y_i\right] d\phi_1 d\phi_2 d\phi_3 - 3\pi^3 .$$

(54) Hence $$\frac{dP}{dT} = \pi^3\left[\frac{3}{T} - \frac{E}{NkT^2}\right]$$, or

(55) $$E = -\frac{NkT^2}{\pi^3}\frac{dP}{dT} + 3NkT .$$ And

(56) $$C_V = \frac{dE}{dT} = \frac{Nk}{\pi^3}\left[3\pi^3 - T^2\frac{d^2P}{dT^2} - 2T\frac{dP}{dT}\right].$$

By the Mittag-Leffler Theorem(12)

(12) Whittaker, E. T. and Watson, G. N., A Course of Modern Analysis, Cambridge University Press, pp.134-140, 1920.

$$(57)\quad \frac{\sinh y}{y} = \frac{\sin(iy)}{iy} = \prod_{n=1}^{\infty}\left[\left(1-\frac{iy}{n\pi}\right)e^{\frac{iy}{n\pi}}\right]\left[\left(1+\frac{iy}{n\pi}\right)e^{-\frac{iy}{n\pi}}\right]$$

$$= \prod_{n=1}^{\infty}\left(1+\frac{y^2}{n^2\pi^2}\right) \cdot \quad \text{Therefore}$$

$$(58)\quad \rho = \tfrac{1}{2}\iiint_{\text{Br. zone}}\left\{\sum_{n=1}^{\infty}\ln\left[1+\frac{1}{n^2}\sum_{i=1}^{3}\left(\frac{y_i}{\pi}\right)^2+\frac{1}{n^4}\sum_{i=1}^{3}\left(\frac{y_i}{\pi}\right)^4 + \frac{1}{n^6}\sum_{i=1}^{3}\left(\frac{y_i}{\pi}\right)^6\right]\right\} d\phi_1 d\phi_2 d\phi_3 .$$

THE MODIFICATION OF THE FIRST BRILLOUIN ZONE

Integration over the Brillouin Zone would be very difficult, because of the limits. Portions of the zone may be translated to give simple limits. The zone is cut up into octants about the x, y, and z axes as appears in Fig. 9.

Let $\vec{\sigma}$ and $\vec{\sigma}'$ denote the wave vector for the eight parts of the Brillouin zone before translation and after translation, respectively.

Writing

(59) $\vec{\sigma} = \sigma_1 \vec{b}_1 + \sigma_2 \vec{b}_2 + \sigma_3 \vec{b}_3$ and

(60) $\vec{\sigma}' = \sigma_1' \vec{b}_1 + \sigma_2' \vec{b}_2 + \sigma_3' \vec{b}_3$, we obtain for the eight parts:

(61)

(1)	$0 \leq \sigma_1 \leq \frac{1}{2}$;	$0 \leq \sigma_2 \leq \frac{1}{2}$;	$0 \leq \sigma_3 \leq \frac{1}{2}$
(2)	$0 \leq \sigma_1 \leq \frac{1}{2}$;	$-\frac{1}{2} \leq \sigma_2 \leq 0$;	$0 \leq \sigma_3 \leq \frac{1}{2}$
(3)	$0 \leq \sigma_1 \leq \frac{1}{2}$;	$-\frac{1}{2} \leq \sigma_2 \leq 0$;	$-\frac{1}{2} \leq \sigma_3 \leq 0$
(4)	$0 \leq \sigma_1 \leq \frac{1}{2}$;	$0 \leq \sigma_2 \leq \frac{1}{2}$;	$-\frac{1}{2} \leq \sigma_3 \leq 0$
(5)	$-\frac{1}{2} \leq \sigma_1 \leq 0$;	$0 \leq \sigma_2 \leq \frac{1}{2}$;	$0 \leq \sigma_3 \leq \frac{1}{2}$
(6)	$-\frac{1}{2} \leq \sigma_1 \leq 0$;	$-\frac{1}{2} \leq \sigma_2 \leq 0$;	$0 \leq \sigma_3 \leq \frac{1}{2}$
(7)	$-\frac{1}{2} \leq \sigma_1 \leq 0$;	$-\frac{1}{2} \leq \sigma_2 \leq 0$;	$-\frac{1}{2} \leq \sigma_3 \leq 0$
(8)	$-\frac{1}{2} \leq \sigma_1 \leq 0$;	$0 \leq \sigma_2 \leq \frac{1}{2}$;	$-\frac{1}{2} \leq \sigma_3 \leq 0$

(62)

(1)	$0 \leq \sigma_1' \leq \frac{1}{2}$;	$0 \leq \sigma_2' \leq \frac{1}{2}$;	$0 \leq \sigma_3' \leq \frac{1}{2}$
(2)	$0 \leq \sigma_1' \leq \frac{1}{2}$;	$\frac{1}{2} \leq \sigma_2' \leq 1$;	$0 \leq \sigma_3' \leq \frac{1}{2}$
(3)	$0 \leq \sigma_1' \leq \frac{1}{2}$;	$\frac{1}{2} \leq \sigma_2' \leq 1$;	$\frac{1}{2} \leq \sigma_3' \leq 1$
(4)	$0 \leq \sigma_1' \leq \frac{1}{2}$;	$0 \leq \sigma_2' \leq \frac{1}{2}$;	$\frac{1}{2} \leq \sigma_3' \leq 1$
(5)	$\frac{1}{2} \leq \sigma_1' \leq 1$;	$0 \leq \sigma_2' \leq \frac{1}{2}$;	$0 \leq \sigma_3' \leq \frac{1}{2}$
(6)	$\frac{1}{2} \leq \sigma_1' \leq 1$;	$\frac{1}{2} \leq \sigma_2' \leq 1$;	$0 \leq \sigma_3' \leq \frac{1}{2}$
(7)	$\frac{1}{2} \leq \sigma_1' \leq 1$;	$\frac{1}{2} \leq \sigma_2' \leq 1$;	$\frac{1}{2} \leq \sigma_3' \leq 1$
(8)	$\frac{1}{2} \leq \sigma_1' \leq 1$;	$0 \leq \sigma_2' \leq \frac{1}{2}$;	$\frac{1}{2} \leq \sigma_3' \leq 1$

Hence

(63) (1) $\vec{\sigma}' = \vec{\sigma}$ (5) $\vec{\sigma}' = \vec{\sigma} + \vec{b}_1$

(2) $\vec{\sigma}' = \vec{\sigma} + \vec{b}_2$ (6) $\vec{\sigma}' = \vec{\sigma} + \vec{b}_1 + \vec{b}_2$

(3) $\vec{\sigma}' = \vec{\sigma} + \vec{b}_2 + \vec{b}_3$ (7) $\vec{\sigma}' = \vec{\sigma} + \vec{b}_1 + \vec{b}_2 + \vec{b}_3$

(4) $\vec{\sigma}' = \vec{\sigma} + \vec{b}_3$ (8) $\vec{\sigma}' = \vec{\sigma} + \vec{b}_1 + \vec{b}_3$

(64) For (1) & (5): $0 \le \sigma_1' \le 1;\ 0 \le \sigma_2' \le \tfrac{1}{2};\ 0 \le \sigma_3' \le \tfrac{1}{2}$

For (2) & (6): $0 \le \sigma_1' \le 1;\ \tfrac{1}{2} \le \sigma_2' \le 1;\ 0 \le \sigma_3' \le \tfrac{1}{2}$

For (3) & (7): $0 \le \sigma_1' \le 1;\ \tfrac{1}{2} \le \sigma_2' \le 1;\ \tfrac{1}{2} \le \sigma_3' \le 1$

For (4) & (8): $0 \le \sigma_1' \le 1;\ 0 \le \sigma_2' \le \tfrac{1}{2};\ \tfrac{1}{2} \le \sigma_3' \le 1$

(65) For (1) & (5) & (2) & (6): $0 \le \sigma_1' \le 1;\ 0 \le \sigma_2' \le 1;\ 0 \le \sigma_3' \le \tfrac{1}{2}$

For (3) & (7) & (4) & (8): $0 \le \sigma_1' \le 1;\ 0 \le \sigma_2' \le 1;\ \tfrac{1}{2} \le \sigma_3' \le 1$

(66) For all segments: $0 \le \sigma_1' \le 1;\ 0 \le \sigma_2' \le 1;\ 0 \le \sigma_3' \le 1$

Therefore, the new figure is a parallelepiped of edges $|\vec{b}_1|$, $|\vec{b}_2|$, $|\vec{b}_3|$. The integration limits for the σ's are now from 0 to 1.

The function P may be expressed as a function of F, G, and H which are functions of the cosines of the ϕ's:

(67) $$P = \tfrac{1}{2} \iiint_{\substack{\text{Br.}\\ \text{zone}}} \left\{ \sum_{n=1}^{\infty} \ln \left[1 + \frac{1}{n^2} \sum_{i=1}^{3} \left(\frac{y_i}{\pi}\right)^2 + \frac{1}{n^4} \sum_{i=1}^{3} \left(\frac{y_i}{\pi}\right)^4 + \frac{1}{n^6} \sum_{i=1}^{3} \left(\frac{y_i}{\pi}\right)^6 \right] \right\} d\phi_1 d\phi_2 d\phi_3$$

$$= \tfrac{1}{2} \sum_{n=1}^{\infty} \iiint_{\substack{\text{Br.}\\ \text{zone}}} \ln \left[1 + \left(\frac{F}{n^2} + \frac{G}{n^4} + \frac{H}{n^6} \right) \right] d\phi_1 d\phi_2 d\phi_3$$

The variables ϕ_1, ϕ_2, ϕ_3 were changed to σ_1, σ_2, σ_3 using equations (32), so that

$$(68)\quad d\phi_1\, d\phi_2\, d\phi_3 = J\left(\frac{\phi_1\phi_2\phi_3}{\sigma_1\sigma_2\sigma_3}\right) d\sigma_1\, d\sigma_2\, d\sigma_3 = 2\pi^3\, d\sigma_1\, d\sigma_2\, d\sigma_3$$

Then the logarithm in the integrand is expanded and the series integrated termwise. The result is:

$$(69)\quad P = 2\pi^3 \sum_{n=1}^{\infty} \frac{1}{n^2}\left\{3\alpha + \frac{3}{4}\gamma\right\} + \pi^3 \sum_{n=1}^{\infty} \frac{1}{n^4}\left\{-8.25\alpha^2 - 3\alpha\gamma + \frac{7}{16}\gamma^2\right\}$$

$$+ \pi^3 \sum_{n=1}^{\infty} \frac{1}{n^6}\left\{-4\alpha^3 + \frac{6577}{64}\alpha^2\gamma - \frac{7}{4}\alpha\gamma^2 + \frac{959}{192}\gamma^3\right\}$$

$$+ \pi^3 \sum \frac{1}{n^8}\left\{15{,}300\,\alpha^4 + 818.81\,\alpha^3\gamma - 4002\,\alpha^2\gamma^2 - 57\alpha\gamma^3 - 7.7\,\gamma^4\right\} + \cdots$$

Using the Bernoulli[13] Numbers to determine the value

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(13) Dwight, H. B., Tables of Integrals and Other Mathematical Data, Macmillan, pp. 10-11, 1947.

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of $\sum_{n=1}^{\infty} \frac{1}{n^{2m}}$, we get

$$(70)\quad \sum_{n=1}^{\infty} \frac{1}{n^{2m}} = \frac{\pi^{2m}\, 2^{2m-1}}{(2m)!}\, B_m$$

$$\sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}; \quad \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90}; \quad \sum_{n=1}^{\infty} \frac{1}{n^6} = \frac{\pi^6}{945};$$

$$\sum_{n=1}^{\infty} \frac{1}{n^8} = \frac{\pi^8}{9450}.$$

Hence

$$(71)\quad P = \frac{1}{3}\pi^5\alpha\left\{3 + .75\frac{\gamma}{\alpha}\right\} + \frac{1}{90}\pi^7\alpha^2\left[-8.25 - 3\frac{\gamma}{\alpha} + .438\left(\frac{\gamma}{\alpha}\right)^2\right\}$$

$$+ \frac{1}{945}\pi^9\alpha^3\left\{-4 + 102.8\frac{\gamma}{\alpha} - 1.75\left(\frac{\gamma}{\alpha}\right)^2 + 5\left(\frac{\gamma}{\alpha}\right)^3\right\}$$

$$+ \frac{1}{9450}\pi^{11}\alpha^4\left\{15{,}300 + 818.8\frac{\gamma}{\alpha} - 4002\left(\frac{\gamma}{\alpha}\right)^2 - 57\left(\frac{\gamma}{\alpha}\right)^3\right.$$

$$\left. - 7.7\left(\frac{\gamma}{\alpha}\right)^4\right\} + \ldots$$

The force constant, α, may be found in terms of the Debye Characteristic Temperature which has been determined for most substances. Since the frequency, ν, is proportional to y the maximum value for y may be found from the secular determinant. This yields

$$(72)\quad y^2 = \frac{\pi^2}{3}\left[F \pm \sqrt{F^2 - 3G}\right]$$ which, when solved for y, gives

(73) ϕ_1, ϕ_2, ϕ_3	y
$0, 0, 0$	0
$\pi/2, \pi/2, \pi/2$	$\pi\sqrt{2\alpha + \gamma}$
π, π, π	$2\pi\sqrt{\alpha}$
$\pi/2, \pi/2, 0$ etc.	$\pi\sqrt{2\alpha + \frac{2}{3}\gamma \pm \frac{1}{3}\sqrt{\gamma^2 - 12\alpha^2}}$
$\pi, \pi, 0$ etc.	0
$\pi, \pi/2, 0$ etc.	$\pi\sqrt{2\alpha + \frac{2}{3}\gamma}$ or $\pi\sqrt{2\alpha}$
$\pi, \pi, \pi/2$ etc.	$\pi\sqrt{2\alpha + \frac{2}{3}\gamma}$ or $\pi\sqrt{2\alpha}$

Thus

(74) $y_m^2 = \left(\frac{h\nu_m}{2kT}\right)^2 = \frac{\Theta^2}{4T^2} = 4\pi^2\alpha$, therefore

(75) $\alpha = \frac{\Theta^2}{16\pi^2 T^2}$ where Θ is the Debye Characteristic Temperature.

THE GENERAL SPECIFIC HEAT EQUATION FOR THE BODY-CENTERED CUBIC LATTICE.

Substituting for α gives

$$(76)\quad P = \frac{\pi^3}{48}\left\{3 + .75\frac{\gamma}{\alpha}\right\}\frac{\Theta^2}{T^2} + \frac{\pi^3}{90\times256}\left\{-8.25 - 3\frac{\gamma}{\alpha} + .438\left(\frac{\gamma}{\alpha}\right)^2\right\}\frac{\Theta^4}{T^4}$$
$$+ \frac{\pi^3}{945\times4096}\left\{-4 + 102.8\frac{\gamma}{\alpha} - 1.75\left(\frac{\gamma}{\alpha}\right)^2 + 5\left(\frac{\gamma}{\alpha}\right)^3\right\}\frac{\Theta^6}{T^6}$$
$$+ \frac{\pi^3}{9450\times65{,}536}\left\{15{,}300 + 818.8\frac{\gamma}{\alpha} - 4002\left(\frac{\gamma}{\alpha}\right)^2 - 57\left(\frac{\gamma}{\alpha}\right)^3 - 7.7\left(\frac{\gamma}{\alpha}\right)^4\right\}\frac{\Theta^8}{T^8} + \ldots$$

Hence

$$(77)\quad C_V = Nk\left[3 - \frac{1}{24}\left\{3 + .75\frac{\gamma}{\alpha}\right\}\frac{\Theta^2}{T^2} - \frac{1}{1920}\left\{-8.25 - 3\frac{\gamma}{\alpha} + .438\left(\frac{\gamma}{\alpha}\right)^2\right\}\frac{\Theta^4}{T^4} - \frac{1}{129{,}024}\left\{-4 + 102.8\frac{\gamma}{\alpha} - 1.75\left(\frac{\gamma}{\alpha}\right)^2 + 5\left(\frac{\gamma}{\alpha}\right)^3\right\}\frac{\Theta^6}{T^6}$$
$$- \frac{1}{11{,}059{,}200}\left\{15{,}300 + 818.8\frac{\gamma}{\alpha} - 4002\left(\frac{\gamma}{\alpha}\right)^2 - 57\left(\frac{\gamma}{\alpha}\right)^3 - 7.7\left(\frac{\gamma}{\alpha}\right)^4\right\}\frac{\Theta^8}{T^8} + \ldots\right].$$

The convergence graph for the model sample.

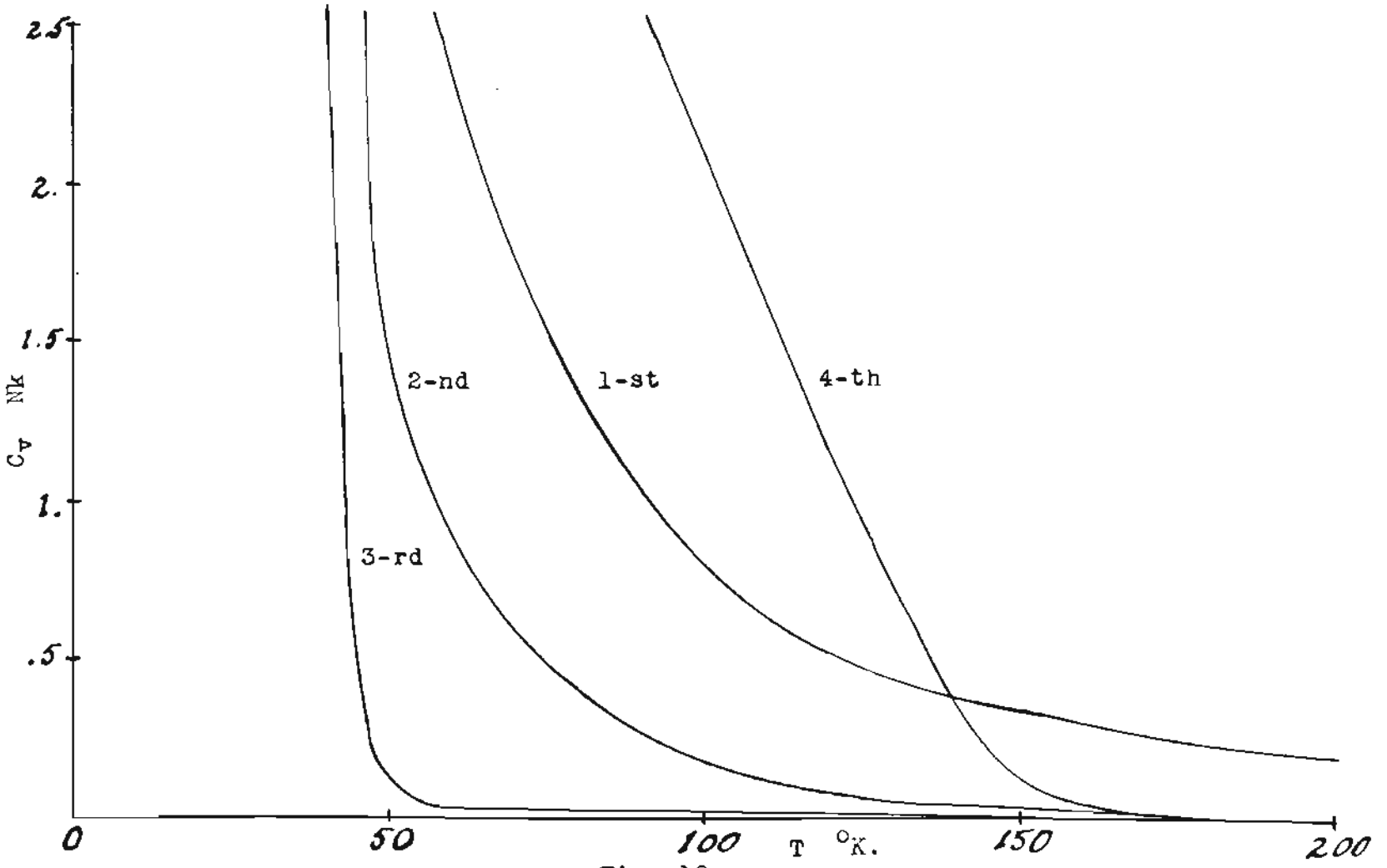

Fig. 10.

THE SPECIFIC HEAT OF A MODEL SAMPLE

No data was available for the ratio of the force constants between next nearest neighbors and neares neighbors in a body-centered cubic crystal. Therefore, a model sample was made up with a ratio of one-eighth and a Debye Characteristic Temperature of 250° K.

From page 25 it can be seen that the ratio of δ/β is the same as the ratio of γ/α. Therefore, in the specific heat equation either ratio may be used.

Using $\Theta = 250°$ K. and $\delta/\beta = \gamma/\alpha = 1/8$ the specific heat equation is

$$(78) \quad C_V = Nk\left[3 - .129\,\frac{\Theta^2}{T^2} + .0045\,\frac{\Theta^4}{T^4} - .000068\,\frac{\Theta^6}{T^6} - .0024\,\frac{\Theta^8}{T^8} + \cdots\right].$$

From an observation of Fig. 10 where the first, second, third, and fourth order terms are plotted it can be seen that the series converges for the first three terms at temperatures as low as 50° K. but because of the behavior of the fourth term the series does not converge at temperatures below the Debye Characteristic Temperature.

CONCLUSIONS

It is concluded that series can be derived for the vibrational energy and specific heat of a body-centered cubic lattice on the basis of the Born-von Kármán theory. These series involve descending powers of the absolute temperature, together with coefficients that can be evaluated from the Debye characteristic temperature and the ratio of the force constants between nearest and next nearest neighbors of the atomic lattice.

For temperatures above roughly one-fifth of the Debye temperature the series for the specific heat converges well so far as its first three terms are concerned. The fourth term, however, turns out to be unexpectedly large, so that the series as a whole may not be suitable for computation. Therefore, unless there exists some undiscovered mistake in the calculations it must be concluded that the Born-von Kármán theory is not correct for the model of a body-centered cubic crystal that was used here.

SUMMARY

A brief discussion of the previous work done and related topics were given with the references.

As an introduction to the discussion of the more complex body-centered cubic lattice, the square lattice and the simple cubic lattice were covered. The aspects of the reciprocal lattice and how it is obtained were given. The Brillouin Zone, which was used to restrict the wave length and frequency, was shown, as was the method of obtaining it.

The potential energy equations were obtained and used to obtain the equations of motion. The secular determinant was formed from the equations of motion and then solved for the $\sqrt{}$'s in terms of the ϕ's. The energy was developed and used in obtaining the specific heat.

The specific heat was calculated for a model sample, and curves were drawn to show the convergence of the series for the specific heat.

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