A thesis

entitled

THE LATTICE DYNAMICS OF HEXAGONAL
CLOSE PACKED METALS

by

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Abstract

This thesis describes the theory of lattice dynamics in a generalised form. The theory is then applied more specifically to materials with hexagonal close-packed structure. In particular the phonon dispersion relations and the frequency spectra are calculated for Beryllium, Magnesium and Zinc using a Born von Kármán model. The results from this model which includes a combination of central and angular forces out to third nearest neighbours are compared with previous experimental and theoretical results. Possible extensions of the model and its limitations are then discussed.

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Chapter 1

Introduction

In a crystalline solid the atoms execute small oscillations about their equilibrium positions as a result of thermal fluctuations or, at the absolute zero, as a result of the zero-point motion. The influence of these lattice vibrations on the thermodynamic properties of solids has been the subject of considerable study since it is the density of the normal modes of vibration which determine many of the macroscopic thermal properties of a crystal. For example the specific heat at constant volume is related to the distribution of normal modes, $g(\nu)$, by

$$C_v = k \int_0^{\infty} \left(\frac{h\nu}{2kT} \right)^2 \frac{g(\nu) d\nu}{\sinh^2\left(\frac{h\nu}{2kT}\right)} \quad (1.1)$$

Here ν and T are respectively the frequency of a normal mode and the absolute temperature. k and h are Boltzmann's and Planck's constants.

In only comparatively few instances is it possible to infer the frequencies and other characteristics of the modes from experimental measurements and consequently much effort has been made to construct theoretical models which give an accurate description of the normal modes of vibration of a structure. The classical theory of lattice vibrations is due to Born and his collaborators (see Born and Huang [1] and references cited therein) and has been applied to molecular, ionic, covalent and metallic

crystals with varying degrees of success. The theory of lattice vibrations is discussed in detail in Chapter 2. In the Born theory it is assumed that the potential energy of a crystal in which the atoms are given small displacements from their equilibrium positions can be expanded as a power series involving the displacements, u , of the nuclei. The actual form of the potential depends on the type of bonding or interatomic force. Thus, for example the inert gas solids can be represented by a Lennard-Jones potential of the form

$$\phi(r) = \frac{A}{r^6} + \frac{B}{r^{12}} \quad (1.2)$$

or alternatively by

$$\phi(r) = \frac{A}{r^6} + Be^{-r/\rho}, \quad (1.3)$$

the first term representing the Van der Waals attraction whilst the second term represents an overlap repulsion. Similarly with ionic solids the potential is often written

$$\phi(r) = \frac{A}{r} + \frac{B}{r^n} \quad (n \approx 12) \quad (1.4)$$

or
$$\phi(r) = \frac{A}{r} + Be^{-r/\rho}, \quad (1.5)$$

where the first term represents the Coulombic attraction. However, for covalent and metallic crystals the interatomic potentials are not so well known and it has been customary to use force constant models for these materials, that is, to regard the nuclei to be connected together by springs, the spring constants depending on the relative positions of the nuclei.

Before the theory of lattice vibrations is discussed, a brief summary of the previous work on force constants is given. Begbie and Born [2] in their paper "Thermal scattering of X-rays by crystals" (1945) presented a generalised form of lattice dynamics without any assumption about the nature of the atomic forces. Begbie [3] in a subsequent paper applied the results to the face-centred cubic and the hexagonal close packed lattices, assuming that only first neighbour atoms act on one another. Prior to this the existing literature, in particular the book "Atomtheorie des festen Zustandes" (Born 1923) [4], had developed the theory assuming central forces. Central force interactions have been applied to a body-centred cubic lattice by Fine [5] and to a face-centred cubic lattice by Leighton [6]. Their models assume interactions only to the second nearest neighbour atoms. Both these cases are discussed by Jules de Launay [7].

The lattice dynamics of hexagonal close packed metals has been investigated by Slutsky and Garland [8], using a central force model out to third nearest neighbour atoms. In recent papers Metzbowler [9,10,11] has discussed the lattice dynamics of the hexagonal close packed metals Beryllium, Magnesium and Zinc. In his work, Metzbowler assumes an axially symmetric force model with interactions extending over three sets of nearest neighbours. In addition it is assumed that the angular force on the nearest neighbours in the basal plane is set equal to zero. In a preliminary study of Metzbowler's papers it was realised that there was a serious limitation in his calculations and errors in some of the algebraic expressions. It has been the object of the work described in Chapter

3 to construct a force constant model which gives an accurate representation of the harmonic properties of Beryllium, Magnesium and Zinc. The results are discussed in Chapter 4.

An alternative approach to the theory of lattice dynamics of metals is Sham's [12] formulation of the problem using pseudo-potential methods. The pseudo-potential equation, which is formally the same as the Schrödinger equation for a free-electron gas with a perturbing potential, involves the conduction-band energies for which the previous models discussed do not make any allowances. Pindor and Pynn [13] have extended the calculations of pseudo-potentials and applied them to Magnesium. The reader is referred to Harrison [14] for a more detailed account of pseudo-potentials.

Chapter 2

2.1. The Lattice

In this chapter the theory of Lattice Dynamics is developed for an arbitrary crystal structure using a Born-von Kármán model (see Born and Huang, [1]). The notation used in the following chapters is easily introduced by considering a Bravais lattice, which is built up from three basic vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$. The lattice points,

$$\vec{r} = s_1 \vec{a}_1 + s_2 \vec{a}_2 + s_3 \vec{a}_3, \quad (s_1, s_2, s_3 \text{ are } + \text{ ve or } - \text{ ve integers}) \quad (2.1)$$

occupy the corners of the lattice cells which are parallelepipeds bounded by the edges $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$. s_1 , s_2 and s_3 are the cell indices. Every lattice site represents an atomic position in the crystal under consideration.

In general a crystal structure consists of a number of interpenetrating Bravais lattices of identical structures (i.e. with identical basic vectors). Therefore within a lattice cell an atom from every constituent Bravais lattice is found. If there are several atoms per unit cell then there exists a lattice with a basis. As a simple lattice is considered as the periodic repetition of a single point, then a complex lattice can be thought of as the repetitions of the points, in the basis, as a group.

So the position vectors of any of the atoms within a crystal lattice containing n atoms per constituent cell may be written as

$$\underline{x}(\underline{s};\alpha) = \underline{s} + \underline{b}(\alpha) , \quad (2.2)$$

where the base index α has the values $1 \dots n$.

The interatomic pairwise potential, ϕ , is defined at the lowest eigenvalue of the electronic energy for fixed atoms in positions near to the regular spacing of the lattice. It is assumed to be a function of the atomic positions. If, due to lattice vibrations, the atoms are displaced from their equilibrium positions $\underline{x}(\underline{s};\alpha)$ by a distance $\underline{u}(\underline{s};\alpha)$, then the potential energy Φ for the disturbed state is given by

$$\Phi = \frac{1}{2} \sum_{\substack{\underline{s} \neq \underline{s}' \\ \underline{\alpha}, \underline{\alpha}'}} \phi \{ \underline{x}(\underline{s} - \underline{s}'; \alpha, \alpha') + \underline{u}(\underline{s};\alpha) - \underline{u}(\underline{s}';\alpha') \} , \quad (2.3)$$

where $\underline{x}(\underline{s} - \underline{s}'; \alpha, \alpha') = \underline{x}(\underline{s};\alpha) - \underline{x}(\underline{s}';\alpha')$.

2.2. The Harmonic Approximation

By making the assumption that the lattice vibrations are small, the potential function Φ is written as a Taylor's series in the atomic displacements. Equation (2.3) then becomes

$$\begin{aligned} \Phi = & \Phi_0 + \sum_{\underline{s}, \alpha} \frac{\delta \Phi}{\partial x_j(\underline{s};\alpha)} \cdot u_j(\underline{s};\alpha) \\ & + \frac{1}{2} \sum_{\substack{\underline{s}, \underline{s}' \\ \underline{\alpha}, \underline{\alpha}'}} \frac{\partial^2 \Phi}{\partial x_j(\underline{s};\alpha) \partial x_k(\underline{s}';\alpha')} \cdot u_j(\underline{s};\alpha) \cdot u_k(\underline{s}';\alpha') \dots \end{aligned} \quad (2.4)$$

The cartesian components of the position vectors are denoted by the suffixes j and k etc., where Einstein's summation convention is adopted for Latin suffixes whilst summation over Greek indexes is shown explicitly.

In the harmonic approximation all terms of third or higher orders are neglected with the result that the motion of the lattice can be resolved into independent modes of vibration. Physically the coefficients in the expansion are well defined quantities. The j th component of the force on the atom $\underline{x}(\underline{s};\alpha)$ is given by $-\partial\Phi/\partial x_j(\underline{s};\alpha)$ in the equilibrium configuration. Similarly $-\partial^2\Phi/\partial x_j(\underline{s};\alpha)\partial x_k(\underline{s}';\alpha')$ is, to the first order of accuracy, the j th component of the force on atom $\underline{x}(\underline{s};\alpha)$ due to a unit displacement of atom $\underline{x}(\underline{s}';\alpha')$ in the k th direction. If the atoms at equilibrium positions $\underline{x}^0(\underline{s};\alpha)$ are arbitrarily displaced to $\underline{x}(\underline{s};\alpha)$ then the j th component of the force on the atoms, F_j , is given by the negative derivative of the lattice potential with respect to the displaced positions. The potential expansion (2.4) is substituted into the force equation,

$$F_j = -\partial\Phi/\partial u_j(\underline{s};\alpha) \quad . \quad (2.5)$$

The derivatives of the potential are evaluated at the equilibrium configuration. It will be shown in the next section that the force on the equilibrium configuration is zero and so the remaining term in the harmonic approximation can be equated with the standard force equation

$$F_j = m\ddot{u}_j(\underline{s};\alpha) \quad . \quad (2.6)$$

So the equations of motion of all the atoms can be written as

$$m\ddot{u}_j(\underline{s};\alpha) + \sum_{\underline{s}',\alpha'} \partial^2\Phi/(\partial x_j \partial x_k) \cdot u_k(\underline{s}';\alpha') = 0, \quad (2.7)$$

where m is the mass of the atom.

2.3. Invariance Conditions

In reality the theories used have always to be applied to crystals of finite dimensions, however, the non-uniform conditions near the surface of a finite crystal give rise only to specific surface effects and are irrelevant for the discussion of bulk properties. In order to avoid making superfluous assumptions about the surface conditions, the crystal lattice is considered to be infinitely extended in all directions. The infinite lattice model is essentially an idealization of the conditions inside a finite crystal, where the direct influence of the surface is negligible. The equilibrium condition for an infinite lattice is two fold,

- a) every atom is in equilibrium
- b) the configuration corresponds to vanishing stress.

The potential energy is subject to restrictions arising from certain invariance conditions. If the whole lattice is displaced by a small vector $\underline{d}$ then the potential energy remains unchanged, however from equation (2.4) we have that each atom contributes a change in the potential function of $\partial\Phi/\partial x_i(\underline{s},\alpha) d_i$. Therefore, as the

total change in potential,

$\sum_{\underline{s};\alpha} (\partial\Phi/\partial x_j(\underline{s};\alpha)) d_j$, is zero then

$$\sum_{\underline{s},\alpha} \partial\Phi/\partial x_j(\underline{s};\alpha) = 0 . \quad (2.8)$$

From the periodic condition it is seen that all the first order coefficients are independent of the cell indices $\underline{s}$ and the higher-order coefficients depend only on the relative cell indices $\underline{s} - \underline{s}'$. So the following notation

$$\Phi_{jk}(\underline{s} - \underline{s}'; \alpha, \alpha') = \partial^2\Phi/(\partial x_j(\underline{s};\alpha) \partial x_k(\underline{s}';\alpha')) \quad (2.9)$$

is adopted.

$$\text{Suppose } \Phi_{jk}(\underline{s} - \underline{s}'; \alpha, \alpha') = \Phi_{jk}(\underline{r}; \alpha, \alpha') . \quad (2.10)$$

then the identity can be considered as the force components on the atom $\underline{x}(\underline{r}, \alpha)$ due to an atom on the base, $\underline{x}(\underline{o}, \alpha')$. There is obviously an equal and opposite force at the atom $\underline{x}(-\underline{r}; \alpha')$ due to the atom $\underline{x}(\underline{o}; \alpha)$. So the identity

$$\Phi_{jk}(\underline{s}; \alpha, \alpha') = \Phi_{kj}(-\underline{s}; \alpha', \alpha) \quad (2.11)$$

is satisfied.

The force due to an atom at position $\underline{x}(\underline{s}; \alpha)$ acting on itself, $\Phi_{jk}(\underline{o}; \alpha, \alpha')$, is determined from all the other forces. If the whole lattice is subjected to a rotation then $\ddot{u}_j(\underline{s}, \alpha) = 0$ and from

equation (2.7)

$$\sum_{\underline{s}, \alpha} \Phi_{jk}(\underline{s} - \underline{s}'; \alpha, \alpha') = 0 \quad (2.12)$$

it follows that

$$\Phi_{jk}(0; \alpha, \alpha) = - \sum_{\substack{\underline{s} \neq \underline{s}' \\ \alpha'}} \Phi_{jk}(\underline{s} - \underline{s}'; \alpha, \alpha') \quad (2.13)$$

2.4. Lattice Waves

If the three elementary vectors of the reciprocal lattice are defined as $\underline{b}_1$, $\underline{b}_2$ and $\underline{b}_3$ such that

$$\underline{a}_\alpha \cdot \underline{b}_\beta = \delta_{\alpha\beta} \quad (\delta_{\alpha\beta} = 1 \text{ if } \alpha = \beta, 0 \text{ if } \alpha \neq \beta) \quad , \quad (2.14)$$

and any reciprocal lattice vector is given by

$$\underline{g} = 2\pi n_1 \underline{b}_1 + 2\pi n_2 \underline{b}_2 + 2\pi n_3 \underline{b}_3 \quad , \quad (2.15)$$

then

$$\underline{s} \cdot \underline{g} = 2\pi n_1 s_1 + 2\pi n_2 s_2 + 2\pi n_3 s_3 \quad . \quad (2.16)$$

So, if $\underline{s}$ is a lattice point (s_j integers) and $\underline{g}$ is a point on the reciprocal lattice (n_j integers), then the scalar product $\underline{s} \cdot \underline{g}$ is a multiple of 2π . Therefore $e^{i\underline{g} \cdot \underline{s}}$ is periodic in the reciprocal lattice.

Using the notation described by the expression (2.9) the

equations of motions of the atoms (2.7) can be written thus,

$$m\ddot{u}_j(\underline{s};\alpha) + \sum_{\underline{s}';\alpha'} \phi_{jk}(\underline{s} - \underline{s}';\alpha,\alpha') u_k(\underline{s}';\alpha') = 0 \quad (2.17)$$

A Fourier Transform of the potential terms in the above equation is given below,

$$\Lambda_{jk}(\underline{q};\alpha,\alpha') = \sum_{\underline{s}} \phi_{jk}(\underline{s};\alpha,\alpha') e^{i\underline{q} \cdot \underline{s}} \quad (2.18)$$

A standard wave solution can be used to describe the lattice displacements, such that

$$u_j(\alpha) = A_j(\alpha) \exp[-i(\underline{q} \cdot \underline{s} - \omega t)] \quad (2.19)$$

Substituting expressions (2.18) and (2.19) into equation (2.17) results in the following set of simultaneous equations, described by

$$m\omega^2 A_j(\alpha) = \sum_{\alpha'} \Lambda_{jk}(\underline{q};\alpha,\alpha') A_k(\alpha') \quad (2.20)$$

where ω is the angular frequency of the wave.

$\Lambda_{jk}(\underline{q};\alpha,\alpha')$, considered as a function of the two sets of

$\Lambda_{jk}(\underline{q};\alpha,\alpha')$, considered as a function of the two sets of

variables (j,α) and (k,α') , is an element of the dynamical matrix

$\Lambda(\underline{q})$ which can be decomposed into submatrices $\Lambda(\underline{q};\alpha,\alpha')$,

where

$$\Lambda(\underline{q}) = \begin{bmatrix} \Lambda(\underline{q};1,1) & \Lambda(\underline{q};1,2) & \dots\dots & \Lambda(\underline{q};1,N) \\ \Lambda(\underline{q};2,1) & \Lambda(\underline{q};2,2) & \dots\dots & \Lambda(\underline{q};2,N) \\ \dots\dots & \dots\dots & \dots\dots & \dots\dots \\ \Lambda(\underline{q};N,1) & \Lambda(\underline{q};N,2) & \dots\dots & \Lambda(\underline{q};N,N) \end{bmatrix} \quad (2.21)$$

Each of these elements can be reduced to a (3×3) matrix, where

$$\Lambda(\underline{q};\alpha,\alpha') = \begin{bmatrix} \Lambda_{11}(\alpha,\alpha') & \Lambda_{12}(\alpha,\alpha') & \Lambda_{13}(\alpha,\alpha') \\ \Lambda_{21}(\alpha,\alpha') & \dots\dots\dots & \dots\dots\dots \\ \Lambda_{31}(\alpha,\alpha') & \dots\dots\dots & \dots\dots\dots \end{bmatrix} \quad (2.22)$$

As α has any value from 1 to N and j has values 1 to 3, then equation (2.20) contains $3N$ linear homogeneous equations. In order for this set of simultaneous equations to yield non trivial solutions, the determinant of the coefficients must equal zero. The resulting secular determinant is

$$| \Lambda(\underline{q}) - m\omega^2 I | = 0 \quad , \quad (2.23)$$

where I is a unit matrix.

The complex conjugate

$$\Lambda_{ij}^* (\underline{q};\alpha,\alpha') = \sum_{\underline{s}} \Phi_{ij} (\underline{s};\alpha,\alpha') e^{-i\underline{q} \cdot \underline{s}} \quad (2.24)$$

can be written as $\sum_{\underline{s}} \Phi_{ji} (-\underline{s};\alpha',\alpha) e^{-i\underline{q} \cdot \underline{s}}$

using the identity given in equation (2.11). If the substitution $\underline{s}' = -\underline{s}$ is then made

$$\begin{aligned}\Lambda_{ij}^* (\underline{q}; \alpha, \alpha') &= \sum_{\underline{s}} \phi_{ji} (\underline{s}'; \alpha', \alpha) e^{i\underline{q} \cdot \underline{s}'} \\ &= \Lambda_{ji} (\underline{q}; \alpha', \alpha)\end{aligned}\quad (2.25)$$

Equation (2.25) shows that the matrix is Hermitian and therefore all the solutions of ω^2 are real. This means that the vibrational frequencies given by $\nu = (\omega^2/4\pi)^{\frac{1}{2}}$ must be either real or purely imaginary. In order that ω^2 is positive so that the frequencies are real, the principal minors of the matrix $\Lambda_{ij}(\underline{q}; \alpha, \alpha')$ must all be positive.

In the method of Long Waves, q is set very small so that the wave length is large compared with the atomic spacings and the crystal responds as a continuum. This enables the equations of motion to be compared with the amplitude of elastic waves in ordinary elasticity theory. The elastic constants can then be obtained in terms of the matrix elements in $\Lambda(\underline{q})$. Using the elastic constants and additional data such as phonon frequencies at selected points in the Brillouin zone the matrix elements can be analysed solely in terms of the reciprocal lattice vector $\underline{q}$. By taking a reciprocal lattice direction specified by $\underline{q}$, the frequency of the lattice waves propagated through the crystal in the direction $\underline{q}$ may be compared to reciprocal wave vectors in that direction; i.e. the phonon dispersion curves can be found.

In equation (2.16) it has been shown that $\underline{s} \cdot \underline{q}$ is some

multiple of 2π . If we consider a finite crystal containing $n = M_1 \cdot M_2 \cdot M_3$ atoms and apply periodic boundary conditions then

$$\left. \begin{aligned} M_1 s_{11} q_1 &= \text{multiple of } 2\pi \\ M_2 s_{22} q_2 &= \text{multiple of } 2\pi \\ M_3 s_{33} q_3 &= \text{multiple of } 2\pi \end{aligned} \right\} \quad (2.26)$$

When considering the reciprocal lattice cell nearest the origin we have

$$-\frac{\pi}{M_\alpha} \leq s_\alpha q_\alpha \leq \frac{\pi}{M_\alpha} \quad \alpha = 1, 2, 3 \text{ and is not summed } (2.27)$$

Thus there are exactly $M_1 \cdot M_2 \cdot M_3$ distinct $\underline{q}$ vectors in the first Brillouin zone.

Suppose a wave vector $\underline{q}$ exists such that

$$\underline{q} = \underline{g} + \underline{q}' \quad , \quad (2.28)$$

where $\underline{g}$ is some reciprocal lattice vector and $\underline{q}'$ is another vector, then the value of $\underline{g}$ can always be chosen to make $|\underline{q}'|$ as small as possible. This means $\underline{q}'$ lies nearer to the origin than to any other sites of the reciprocal lattice. Therefore because of the periodicity of the lattice it is evident that any point $\underline{q}$ in reciprocal space can be reduced to a point in the first Brillouin zone.

The secular determinant (2.23) is too complicated for an easy general solution, but the $3N$ roots in v^2 can be identified

physically in the long - wavelength limit.

The situation in which there is one atom per unit cell and therefore three roots in v^2 is considered. In effect an elastic continuum is being dealt with, whose structure is too fine to be significant in the dynamics of long waves. It is known that in such a continuum three types of acoustic waves of different velocities may be propagated. The essential difference between these three acoustic modes is in the nature of their polarization. In an isotropic continuum one mode is longitudinally polarized. This means that the displacement vector of each atom is along the direction of propagation of the wave. The other two modes are of the same velocity and transversely polarized, in other words the atoms move in the planes normal to the wave vector. However, a crystal structure is ~~not~~ ^{never} isotropic in its macroscopic elastic properties, so the velocity of a wave will depend on the direction of propagation. In the more complicated case where there are N atoms per unit cell $3(N - 1)$ optical modes are found. This is because optical modes involve displacements of the atoms within the cell in different directions, whereas acoustic modes are due to the atoms vibrating in the same direction.

The classification of the modes into either transverse or longitudinal can be rather misleading as it is not necessary for the polarization vector to be perpendicular to, or parallel to the wave propagation vector.

The relation between v and q is linear near $q = 0$, with the

slope equal to the corresponding macroscopic sound velocity. The elastic constants can also be determined from the slope. As the boundary of the Brillouin zone is approached dispersion takes place. The dispersion is necessary to satisfy the condition that the whole pattern of roots of Λ , as a function of $\underline{q}$ in reciprocal space, is continuous and has the periodicity of the reciprocal lattice.

2.5. The Method of Long Waves

For small values of $\underline{q}$ equation (2.20) can be solved by a perturbation method originally due to Born [4]. The corresponding solutions, which represent lattice waves of large wave-length, enable the elastic constants to be expressed in terms of the matrix elements $\Lambda(\underline{q})$.

One point should be considered before the perturbation method is developed. There are $3N$ solutions to equation (2.20) and it is reasonable to expect that if $\underline{q}$ is varied continuously then the $3N$ branches of the dispersion curve will also vary in a continuous way. This is generally true except in the immediate neighbourhood of the point $\underline{q} = 0$. By considering the simple case of elastic waves in an isotropic medium it can be shown that the dependence of the solutions on the parameter $\underline{q}$ is not regular at the point $\underline{q} = 0$.

It is known that for any wave vector $\underline{q}$ there are two transverse waves and one longitudinal wave. This means that as the point $\underline{q} = 0$ is approached through the $\underline{q}$ -values all pointing in the same direction, the polarization vectors of the three solutions remain throughout

respectively parallel and perpendicular to the given direction. The limits of the polarization vectors are therefore different if the point $\underline{q} = 0$ is approached from different directions. As no unique limit exists for the solutions $\underline{q} = 0$, the solutions of ω cannot be represented in the form of Taylor's series in the components q_1 , q_2 , and q_3 as independent parameters.

By considering only a one-dimensional continuum of solutions which belong to the same direction, the difficulties may be overcome. Using the magnitude $|\underline{q}|$ in the above case it is found that the solutions do vary continuously with $|\underline{q}|$ down to the point $\underline{q} = 0$. The perturbation method is therefore developed by writing the wave vector as

$$\underline{q} = \epsilon \underline{q} \quad (2.29)$$

and expanding all quantities depending on the wave vector with respect to ϵ . This form of expansion is equivalent to an expansion with respect to the magnitude of the wave vector for a fixed direction of the latter. The expansion parameter ϵ can be put equal to unity after the expansion has been carried out.

By expanding equation (2.18) with respect to ϵ , the following expression is obtained

$$\Lambda_{jk}(\epsilon \underline{q}; \alpha, \alpha') = \Lambda_{jk}^{(0)}(\alpha, \alpha') + \Lambda_{jk}^{(1)}(\alpha, \alpha') + \Lambda_{jk}^{(2)}(\alpha, \alpha') \quad , \quad (2.30)$$

where

$$\Lambda_{jk}^{(0)}(\alpha, \alpha') = \sum_{\underline{s}} \Phi_{jk}(\underline{s}; \alpha, \alpha') , \quad (2.31)$$

$$\Lambda_{jk}^{(1)}(\alpha, \alpha') = i\epsilon \sum_{\underline{s}} \sum_{\ell} \Phi_{jk}(\underline{s}; \alpha, \alpha') x_{\ell}(\underline{s}; \alpha, \alpha') q_{\ell} \quad (2.32)$$

and

$$\Lambda_{jk}^{(2)}(\alpha, \alpha') = - \frac{\epsilon^2}{2} \sum_{\underline{s}} \sum_{\ell n} \Phi_{jk}(\underline{s}; \alpha, \alpha') x_{\ell}(\underline{s}; \alpha, \alpha') x_n(\underline{s}; \alpha, \alpha') q_{\ell} q_n \quad (2.33)$$

Equation (2.20) can be written in the more compact form

$$\Omega \underline{A} = \Lambda(q) \underline{A} , \quad (2.34)$$

where $\Omega = \epsilon \omega^2$ and $\underline{A}$ is a one-column matrix,

$$\underline{A} = \{ A_1^{(1)} , A_2^{(1)} , A_3^{(1)} , A_1^{(2)} \dots A_2^{(N)} , A_3^{(N)} \} . \quad (2.35)$$

Ω and $\underline{A}$ can also be expanded in the above way such that

$$\Omega = \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} + \dots \quad (2.36)$$

$$\text{and} \quad \underline{A} = \underline{A}^{(0)} + \underline{A}^{(1)} + \underline{A}^{(2)} + \dots \quad (2.37)$$

The following set of equations is obtained from a comparison of equal powers in equation (2.34),

$$\Omega^{(0)} \underline{A}^{(0)} = \Lambda^{(0)} \underline{A}^{(0)} \quad (2.38)$$

$$\Omega^{(0)} \underline{A}^{(1)} + \Omega^{(1)} \underline{A}^{(0)} = \Lambda^{(0)} \underline{A}^{(1)} + \Lambda^{(1)} \underline{A}^{(0)} \quad (2.39)$$

$$\Omega^{(0)} \underline{A}^{(2)} + \Omega^{(1)} \underline{A}^{(1)} + \Omega^{(2)} \underline{A}^{(0)} = \Lambda^{(0)} \underline{A}^{(2)} + \Lambda^{(1)} \underline{A}^{(1)} + \Lambda^{(2)} \underline{A}^{(0)} . \quad (2.40)$$

These equations must be satisfied for any translation of the crystal as a whole. There are three independent translations

$$u_1(\underline{s};\alpha) , u_2(\underline{s};\alpha) \text{ and } u_3(\underline{s};\alpha) . \quad (2.41)$$

The corresponding $A_j(\alpha)$ are obtained from equation (2.19) for the zero approximation by setting

$$\omega = 0 \text{ and } \underline{q} = 0 . \quad (2.42)$$

This results in the expression for the column matrix

$$\underline{A}^{(0)} = \{u_1(1), u_2(1), u_3(1), u_1(2), u_2(2) \dots u_2(n), u_3(n)\} = \underline{u} . \quad (2.43)$$

As both $\underline{\Omega}^{(0)}$ and $\underline{\Omega}^{(1)}$ are zero because ω^2 is of the second order in ϵ , the first order equation is reduced to

$$\underline{\Lambda}^{(0)} \underline{A}^{(1)} = - \underline{\Lambda}^{(1)} \underline{A}^{(0)} . \quad (2.44)$$

So $\underline{A}^{(1)}$ may be expressed in terms of $\underline{A}^{(0)}$ such that

$$\underline{A}^{(1)} = -[\underline{\Lambda}^{(0)}]^{-1} \underline{\Lambda}^{(1)} \underline{A}^{(0)} . \quad (2.45)$$

The second order equation is rearranged so that

$$\underline{\Lambda}^{(0)} \underline{A}^{(2)} = \underline{\Omega}^{(2)} \underline{A}^{(0)} - \underline{\Lambda}^{(1)} \underline{A}^{(1)} - \underline{\Lambda}^{(2)} \underline{A}^{(0)} . \quad (2.46)$$

In order to obtain the solutions of the above equation, the following theorem must be considered. In the s equations given by

$$\sum_{n=1}^s B_{nm} x_n = C_m \quad (m = 1, 2 \dots s) , \quad (2.47)$$

the left and right-hand sides are known respectively as the homogeneous and inhomogeneous parts where x_n are the unknowns. The equations can be solved in the usual way only if B_{mn} is non-singular, i.e. if $|B_{mn}| \neq 0$. If one or more solutions $x_n(j)$ exist for the associated homogeneous equations, obtained by equating the homogeneous part of (2.47) to zero,

$$\sum_{n=1}^S B_{mn} x_n(j) = 0 \quad (2.48)$$

then the matrix is singular. The necessary and sufficient condition for the inhomogeneous equations to be soluble is that

$$\sum_{m=1}^S x_m(j) C_m = 0, \quad (2.49)$$

for all j .

So the solubility equation for (2.46) is

$$\Omega^{(2)} \underline{A}^{(0)} = \Lambda^{(1)} \underline{A}^{(1)} + \Lambda^{(2)} \underline{A}^{(0)}. \quad (2.50)$$

By substituting equations (2.46) and (2.43) into the above equation the following result is obtained

$$\Omega^{(2)} \underline{u} = [\Lambda^{(2)} - \Lambda^{(1)} [\Lambda^{(0)}]^{-1} \Lambda^{(1)}] \underline{u}. \quad (2.51)$$

The explicit expression of (2.51) has the form

$$m\omega^2 u_i = \sum_j \sum_{\lambda\mu} B_{ij\lambda\mu} q_\lambda q_\mu u_j, \quad (2.52)$$

where B is given in terms of the expansions in equations (2.32), (2.33) and (2.34) to be

$$B = \sum_{\underline{s}} \sum_{\alpha, \alpha'} \left\{ \sum_{\underline{s}} \sum_{\alpha_1, \alpha_2} \sum_{\gamma\delta} \phi_{ij}(\underline{s}; \alpha, \alpha_1) x_\lambda(\underline{s}; \alpha, \alpha_1) \right.$$

$$[\Lambda^{(0)} (\alpha_1, \alpha_2)]_{\gamma\delta}^{-1} \phi_{\delta j}(\underline{s}; \alpha_2, \alpha') x_{\mu}(\underline{s}; \alpha_2, \alpha') - \phi_{ij}(\underline{s}; \alpha, \alpha') x_{\lambda}(\underline{s}; \alpha, \alpha') x_{\mu}(\underline{s}; \alpha, \alpha') \} . \quad (2.52a)$$

Now consider the forces acting on a unit volume of an homogeneous elastic solid in which the stresses σ_{ij} and displacements u_i are referred to an arbitrary system of cartesian axes x_i . The forces on the solid are written as

$$\frac{\partial \sigma_{ij}}{\partial x_j} = \rho \frac{\partial^2 u_i}{\partial t^2} , \quad (2.53)$$

assuming there are no body forces. Substituting Hooke's Law

$$\sigma_{ij} = C_{ijkl} \frac{\partial u_k}{\partial x_l} \quad (2.54)$$

into the above equation results in a system of linear partial differential equations of the second order

$$C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l} - \rho \ddot{u}_i = 0 . \quad (2.55)$$

If the displacements are expressed as the wave form (2.19) then equation (2.55) can be written in a form due originally to Christoffel [15]

$$(\Gamma_{ik} - \rho \omega^2 \delta_{ik}) A_k = 0 , \quad (2.56)$$

where the Γ_{ik} are quadratic functions of the lattice vectors q_j with coefficients according to the following table:

$$\begin{array}{ccccccc}
 q_1^2 & q_2^2 & q_3^2 & 2 q_2 q_3 & 2 q_3 q_1 & 2 q_1 q_2 & \\
 \Gamma_{11} & C_{11} & C_{66} & C_{55} & C_{56} & C_{15} & C_{16} \\
 \Gamma_{22} & C_{66} & C_{22} & C_{44} & C_{24} & C_{46} & C_{26} \\
 \Gamma_{33} & C_{55} & C_{44} & C_{33} & C_{34} & C_{35} & C_{45} \\
 \Gamma_{23} & C_{56} & C_{24} & C_{34} & \frac{1}{2}(C_{23} + C_{44}) & \frac{1}{2}(C_{36} + C_{45}) & \frac{1}{2}(C_{25} + C_{46}) \\
 \Gamma_{13} & C_{15} & C_{46} & C_{35} & \frac{1}{2}(C_{36} + C_{45}) & \frac{1}{2}(C_{13} + C_{55}) & \frac{1}{2}(C_{14} + C_{56}) \\
 \Gamma_{12} & C_{16} & C_{26} & C_{45} & \frac{1}{2}(C_{25} + C_{46}) & \frac{1}{2}(C_{14} + C_{56}) & \frac{1}{2}(C_{12} + C_{66})
 \end{array}
 \tag{2.57}$$

The result (2.56) has the form of (2.52) and allows the elastic constants to be equated with terms of the dynamical matrix $\Lambda(q)$.

2.6. Frequency Spectra and Specific Heats.

The frequency spectrum $g(\nu)$ is defined so that $g(\nu) d\nu$ is the number of normal modes in the interval ν to $\nu + d\nu$. By solving the secular determinant,

$$\left| \Lambda(q) - m\omega^2 I \right| = 0, \tag{2.58}$$

at a large number of points within the first Brillouin zone and determining the number of roots that lie within the given frequency intervals, the spectra may be approximated.

For hexagonal close packed metals the matrix $\Lambda(\underline{q})$ is given in terms of 3×3 submatrices A and B as

$$\Lambda(\underline{q}) = \begin{vmatrix} A & B \\ B^* & A \end{vmatrix} . \quad (2.59)$$

In the matrix $\Lambda(\underline{q})$, the submatrix A is seen to be real and symmetrical, B is complex and symmetrical and B^* is the complex conjugate of B. Therefore $\Lambda(\underline{q})$ is an Hermitian matrix. The numerical solutions can be simplified by transforming $\Lambda(\underline{q})$ into a real form. Since the roots of the secular equation, which are eigenvalues of $\Lambda(\underline{q})$, are invariant under a similarity transformation then $|\Lambda^R - m\omega^2 I| = 0$,

$$(2.60)$$

where $\Lambda^R = T^{-1} \Lambda(\underline{q}) T$ (2.61)

Consider $\Lambda(\underline{q})$ as written in terms of the 3×3 symmetric submatrices A and B and let

$$B = B' + B'' i , \quad (2.62)$$

where B' and B'' are real 3×3 matrices. With the choice of T given by

$$T = \frac{1}{\sqrt{2}} \begin{pmatrix} I & iI \\ iI & I \end{pmatrix} , \quad (2.63)$$

where I is the 3×3 unit matrix, the real matrix $\Lambda^R(\underline{q})$ is

$$\Lambda^R = \begin{vmatrix} A - B'' & B' \\ B' & A + B'' \end{vmatrix} . \quad (2.64)$$

The frequency modes, calculated from equation (2.58), are normalized such that

$$\int_0^{\nu_{\max}} g(\nu) d\nu = 1 \quad . \quad (2.65)$$

This is necessary as it is not possible to compute all the normal modes.

The Specific Heat at constant volume can be calculated from a knowledge of frequency spectrum by integrating the expression

$$C_v = k \int_0^{\nu_{\max}} \left(\frac{h\nu}{2kT} \right)^2 \frac{g(\nu) d\nu}{\sinh^2\left(\frac{h\nu}{2kT}\right)} \quad , \quad (2.66)$$

where h is Plank's constant, k is Boltzmann's constant and T is the temperature.

A more sensitive parameter for comparing observed and calculated values of C_v is θ_D and can be obtained from Gopal's tables [16]. Debye's approximation assumes a common maximum value of the frequency, $\nu_{\max}$, for the longitudinal (L) and Transverse (T) branches of a monatomic simple lattice. So instead of requiring

$$q_{\max} = \nu_{\max}(L) V_L = \nu_{\max}(T) V_T \quad , \quad (2.67)$$

where V_L and V_T are the velocities of the wave, the Brillouin zone is set in a different position for the longitudinal and transverse waves by the condition,

$$\nu_{\max} = \frac{q_{\max}}{V_L} (L) = \frac{q_{\max}}{V_T} (T) \quad . \quad (2.68)$$

The Debye Temperature is defined in terms of the maximum frequency of the monatomic lattice by the equation

$$\theta_D = h\nu_{\max}/k \quad . \quad (2.69)$$

Chapter 3

3.1. The Properties of Beryllium, Magnesium and Zinc

In the close packed hexagonal lattice there are two atoms per unit cell. So in equation (2.2) n takes the value 1 or 2. The basis vectors have the following values,

$$\underline{b}(1) = 0, \quad \underline{b}(2) = \frac{1}{3} \underline{a}_1 + \frac{2}{3} \underline{a}_2 + \frac{1}{2} \underline{a}_3, \quad (3.1)$$

where $\underline{a}_1$, $\underline{a}_2$ and $\underline{a}_3$ ($|\underline{a}_1| = |\underline{a}_2| = a$, $|\underline{a}_3| = c$) are the base vectors of the hexagonal lattice. The lattice parameters and elastic constants of Beryllium, Magnesium and Zinc are given in Table 1 below.

Table 1

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	c	a	c/a	
Be	2.99	0.28	0.11	3.42	1.66	3.58	2.28	1.57	Ref.[17]
Mg	0.628	0.259	0.217	0.657	0.181	5.21	3.21	1.63	Ref.[18]
Zn	1.768	0.368	0.552	0.677	0.448	4.94	2.66	1.86	Ref.[19]

The elastic constants are in units of 10^{12} dynes/cm² and the lattice parameters are in angstroms. $\underline{a}_1$ and $\underline{a}_2$ subtend an angle of 120° and $\underline{a}_3$ is perpendicular to the plane containing $\underline{a}_1$ and $\underline{a}_2$.

For convenience the atom at position $\alpha = 1$, $\underline{s} = 0$ is taken as the origin of the lattice. The atom at the origin has six

nearest neighbours. These are defined to be in the same a_1 , a_2 plane and at a distance $|a|$ from the origin. There are six second and six third nearest neighbours at distances of $[(c^2/4) + a^2/3]^{1/2}$ and $[(c^2/4) + 4a^2/3]^{1/2}$ respectively. If $c/a < \left(\frac{8}{3}\right)^{1/2}$ the second nearest neighbours are closer to the atom at the origin than the first nearest neighbours. The two fourth nearest neighbours are situated at a distance c from the origin in the a_3 direction. Table 2 lists the hexagonal co-ordinates of the atoms.

Table 2 Nearest neighbours positions

S_1	S_2	S_3	α	
1	0		1	
-1	0			
0	1			1st neighbours
0	-1			
1	1			
-1	-1			
0	0	-1	2	
0	0	0		
0	-1	-1		2nd neighbours
0	-1	0		
-1	-1	-1		
-1	-1	0		
-1	-2	0	2	
-1	-2	-1		
1	0	0		3rd neighbours
1	0	-1		
-1	0	0		
-1	0	-1		
0	0	-1	1	
0	0	1		4th neighbours

The hexagonal components s_j may be expressed in terms of the components r_j of a cartesian system, where $a_1 = x_1$ and

$$\vec{r} = r_1 \vec{x}_1 + r_2 \vec{x}_2 + r_3 \vec{x}_3 \quad (3.2)$$

The transformation is given by

$$r_j = T_{jk} s_k \quad (3.3)$$

where the transformation matrix T_{jk} is

$$T_{jk} = \begin{bmatrix} 1 & -\frac{1}{2} & 0 \\ 0 & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & c/a \end{bmatrix} \quad (3.4)$$

In the case of ideal closest packing, the general axial ratio c/a has the value of $(8/3)^{1/2} \approx 1.633$. This ideal ratio is closely approximated by Magnesium. Beryllium and Zinc have lower and higher c/a ratios respectively than that of the ideal lattice.

The atomic distances are given in Table 3 for Beryllium, Magnesium and Zinc. The distance of the j th nearest neighbours is denoted by r_j .

Table 3 Nearest neighbour distances

	<u>Be</u>	<u>Mg</u>	<u>Zn</u>
r_1	a	a	a
r_2	$0.974a$	$0.996a$	$1.092a$
r_3	$1.396a$	$1.390a$	$1.481a$
r_4	$1.568a$	$1.624a$	$1.855a$

3.2. The Noncentral Force Model

In the following calculations a noncentral force model is used. This noncentral force consists of a combination of central forces and angular forces. These forces may be distinguished by expressing equation (2.9) as a function of the atomic distances r , such that

$$\phi_{jk} = \frac{\partial}{\partial x_j} \left\{ \frac{\partial r}{\partial x_k} \cdot \frac{\partial \phi}{\partial r} \right\} , \quad (3.5)$$

where $r^2 = \sum_k x_k^2$ and the dashed superscript denotes the position vector $\underline{x}(\underline{s}'; \alpha')$. After manipulation the above equation becomes

$$\phi_{jk} = \delta_{jk} \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{x_j x_k}{r^2} \left(\frac{\partial^2 \phi}{\partial r^2} - \frac{1}{r} \frac{\partial \phi}{\partial r} \right) . \quad (3.6)$$

The central force is given by

$$\frac{\partial^2 \phi}{\partial r^2} = A(\underline{s} - \underline{s}'; \alpha, \alpha') \quad (3.7)$$

and the angular force by

$$\frac{1}{r} \frac{\partial \phi}{\partial r} = B(\underline{s}; \alpha) . \quad (3.8)$$

Therefore equation (3.6) can be written as

$$\begin{aligned} \phi_{jk}(\underline{s} - \underline{s}'; \alpha, \alpha') = & \delta_{jk} B(\underline{s} - \underline{s}'; \alpha, \alpha') + \frac{x_j x_k}{r^2} [A(\underline{s} - \underline{s}'; \alpha, \alpha') \\ & - B(\underline{s} - \underline{s}'; \alpha, \alpha')] , \end{aligned} \quad (3.9)$$

where A and B are defined above.

The central force is assumed to act only along the line joining the two atoms under consideration and it is in this sense a 'radial force'. This force always acts to restore the radial equilibrium distance between the atoms. The model requires one central force constant for each set of nearest neighbours. These force constants are denoted as $A^{(1)}$, $A^{(2)}$, $A^{(3)}$ and $A^{(4)}$ according to the radial distances given in Table 3.

The angular force depends on the angle which the line joining the moving atoms makes with the equilibrium position of the line. Similarly to the central force constants, there are four angular force constants given by $B^{(1)}$, $B^{(2)}$, $B^{(3)}$ and $B^{(4)}$.

If a case is considered when there is only two fold symmetry about the equilibrium line, then two angular force constants should be considered for each set of nearest neighbours. These correspond to the two directions perpendicular to one another and to the central force. However, as a hexagonal close packed lattice is under consideration the latter point is not applicable.

3.3. Long Waves in the H.C.P. Structure

For the hexagonal closed packed structure the relationships between the elastic constants and terms in the diagonal matrix are much simpler than the general case discussed in section 2.5. This simplification arises from the fact that there are only two atoms per unit cell. Consequently equation (2.38)

$$\Omega(0) \underline{A}^{(0)} = \Lambda^{(0)} \underline{A}^{(0)} \quad (3.10)$$

can be written in the form

$$\Lambda_{ij}^{(0)}(1,1) A_j^{(0)}(1) + \Lambda_{ij}^{(0)}(1,2) A_j^{(0)}(2) = 0 \quad . \quad (3.11)$$

From equations (2.12) and (2.31) it can be shown that

$$\Lambda_{ij}^{(0)}(1,1) = - \Lambda_{ij}^{(0)}(1,2) \quad . \quad (3.12)$$

By substituting equation (3.12) into equation (3.11) the following identity emerges,

$$A_j^{(0)}(1) = A_j^{(0)}(2) \quad . \quad (3.13)$$

In the first order approximation equation (2.20) is written as

$$\sum_{\alpha'} \Lambda_{ij}^{(0)}(\alpha, \alpha') A_j^{(1)}(\alpha') + \sum_{\alpha'} \Lambda_{ij}^{(1)}(\alpha, \alpha') A_j^{(0)}(\alpha') = 0 \quad . \quad (3.14)$$

By constructing the matrix elements for the hexagonal close packed structure from equation (2.18), it is found that

$$\Lambda^{(1)}(1,1) = 0 \quad . \quad (3.15)$$

Using the above property and the identity given in equation (3.12) the first order equation can be expressed in the following way.

$$A_j^{(1)}(1) - A_j^{(1)}(2) = - [\Lambda_{ij}^{(0)}(1,1)]^{-1} \Lambda_{ij}^{(1)}(1,2) A_j^{(0)}(2) \quad . \quad (3.16)$$

The second order approximation is written as

$$\Omega^{(2)} \underline{A}^{(0)}(\alpha) = \sum_{\alpha'} \{ \Lambda^{(0)}(\alpha, \alpha') \underline{A}^{(2)}(\alpha') + \Lambda^{(1)}(\alpha, \alpha') \underline{A}^{(1)}(\alpha') \\ \Lambda^{(2)}(\alpha, \alpha') \underline{A}^{(0)}(\alpha') \} . \quad (3.17)$$

By initially giving α the value 1 and using the same properties as in the first order calculation the above equation can be written as

$$\Omega^{(2)} \underline{A}_j^{(0)}(1) = \Lambda_{jk}^{(0)}(1,1) [A_k^{(2)}(1) - A_k^{(2)}(2)] \\ + \Lambda_{jk}^{(1)}(1,2) A_k^{(1)}(2) \\ + \{ \Lambda_{jk}^{(2)}(1,1) + \Lambda_{jk}^{(2)}(1,2) \} A_k^{(0)}(1) . \quad (3.18)$$

Similarly when α has the value 2 equation (3.17) is written as

$$\Omega^{(2)} \underline{A}_j^{(0)}(2) = \Lambda_{jk}^{(0)}(2,1) [A_k^{(2)}(1) - A_k^{(2)}(2)] \\ + \Lambda_{jk}^{(1)}(2,1) A_k^{(1)}(1) \\ + \{ \Lambda_{jk}^{(2)}(2,1) + \Lambda_{jk}^{(2)}(1,1) \} A_k^{(0)}(1) . \quad (3.19)$$

In the zero order approximation it was found that

$$A_j^{(0)}(1) = A_j^{(0)}(2) \quad (3.20)$$

and so consequently

$$\Omega^{(2)} A_j^{(0)}(2) + \Omega^{(2)} A_j^{(0)}(1) = 2\Omega^{(2)} A_j^{(0)}(1) \quad . \quad (3.21)$$

From equation (2.11) it may be shown that

$$\Lambda_{jk}^{(1)}(2,1) = \Lambda_{jk}^{(1)*}(1,2) = -\Lambda_{jk}^{(1)}(1,2) \quad . \quad (3.22)$$

The above equation substituted into equation (3.19) with the identity given in (3.16) results in the following expression

$$\begin{aligned} 2\Omega^{(2)} A_i^{(0)}(1) &= \Lambda_{im}^{(1)}(1,2) [\Lambda_{mn}^{(0)}(1,1)]^{-1} \Lambda_{nk}^{(1)}(1,2) A_k^{(0)}(1) \\ &\quad + 2 \{ \Lambda_{ik}^{(2)}(1,1) + \Lambda_{ik}^{(2)}(1,2) \} A_k^{(0)}(1) \quad . \end{aligned} \quad (3.23)$$

The above equation is compared with the elastic solution

$$m\omega^2 A_i(1) = v_a C_{ijkl} q_j q_l A_k(1) \quad , \quad (3.24)$$

which arises from substituting the wave solution into equation (2.55). v_a is the atomic volume. By equating the two solutions, the following relation between the elastic constants and the matrix elements is obtained.

$$\begin{aligned} v_a C_{ijkl} q_j q_l &= \frac{1}{2} \Lambda_{im}^{(1)}(1,2) [\Lambda_{mn}^{(0)}(1,1)]^{-1} \Lambda_{nk}^{(1)}(1,2) \\ &\quad + \Lambda_{ik}^{(2)}(1,1) + \Lambda_{ik}^{(2)}(1,2) \quad . \end{aligned} \quad (3.25)$$

So by using the force constants given in equation (3.9),
the elastic constants may be written thus:

$$C_{13} = \frac{2}{\sqrt{3}c} \left(\frac{c}{a} \right)^2 \{E(2)/4 + E(3) - (3/2)B - 2B^{(4)}\} . \quad (3.26)$$

$$C_{44} = \frac{2}{\sqrt{3}c} \left(\frac{c}{a} \right)^2 \{E(2)/4 + E(3) + (3/2)B + 2B^{(4)}\} . \quad (3.27)$$

$$C_{33} = \frac{2}{\sqrt{3}c} \left(\frac{c}{a} \right)^2 \left\{ \frac{3}{8} \left(\frac{c}{a} \right)^2 (E(2) + E(3)) + (3/2)B + 2A^{(4)} \right\} . \quad (3.28)$$

$$C_{11} = \frac{2}{\sqrt{3}c} \left\{ \frac{9}{4} [A^{(1)} - B^{(1)}] + E(2)/4 + 4E(3) + 3B^{(1)} + B^{(2)} \right. \\ \left. + 4B^{(3)} - \frac{3}{4} \frac{\alpha^2}{\Lambda_x} \right\} . \quad (3.29)$$

$$C_{12} = \frac{2}{\sqrt{3}c} \left\{ \frac{3}{4} [A^{(1)} - B^{(1)}] + E(2)/12 + \frac{4}{3} E(3) - 3B^{(1)} - B^{(2)} \right. \\ \left. - 4B^{(3)} + \frac{3}{4} \frac{\alpha^2}{\Lambda_x} \right\} . \quad (3.30)$$

where

$$E(2) = \frac{a^2}{r_2^2} [A^{(2)} - B^{(2)}] , \quad E(3) = \frac{a^2}{r_3^2} [A^{(3)} - B^{(3)}] ,$$

$$B = B^{(2)} + B^{(3)} , \quad \alpha = \frac{8}{3} E(3) - \frac{1}{3} E(2)$$

and

$$\Lambda_x = 6B + E(2) + 4E(3) .$$

Similarly Huang's condition [20] for the vanishing of the deviatoric stress tensor S_{ij} , which corresponds to

$$\sum_{\underline{s}, \alpha, \alpha'} x_i(\underline{s}; \alpha, \alpha') x_j(\underline{s}; \alpha, \alpha') \phi'(|\underline{x}(\underline{s}; \alpha)|) = 0, \quad (3.31)$$

can be expressed as

$$3B^{(1)} + B^{(2)} + 4B^{(3)} = \frac{3}{2} \left(\frac{c}{a} \right)^2 \{B^{(2)} + B^{(3)} + \frac{4}{3} B^{(4)}\}. \quad (3.32)$$

This condition forces the velocity of the elastic waves in the [0001] direction, polarized in the [01 $\bar{1}$ 0] direction to be equal to that of the elastic wave in the [01 $\bar{1}$ 0] direction and polarized in the [0001] direction.

3.4. The Phonon Dispersion Relations

For the hexagonal close packed structure the expression for the dynamical matrix given in equation (2.21) reduces to

$$\Lambda(\underline{q}) = \begin{bmatrix} \Lambda_{11}(1,1) & & & \Lambda_{11}(1,2) & & \\ & \Lambda_{22}(1,1) & & & \Lambda_{22}(1,2) & \\ & & \Lambda_{33}(1,1) & & & \Lambda_{33}(1,2) \\ \Lambda_{11}(2,1) & & & \Lambda_{11}(1,1) & & \\ & \Lambda_{22}(2,1) & & & \Lambda_{22}(1,1) & \\ & & \Lambda_{33}(2,1) & & & \Lambda_{33}(1,1) \end{bmatrix}, \quad (3.33)$$

for waves propagated in the [0001] and [01 $\bar{1}$ 0] directions.

Due to the above symmetry, the secular determinant can be factorized into the three separate determinants below;

$$\begin{array}{lcl}
 \text{a)} & \left| \begin{array}{cc} \Lambda_{11}(1,1) - m\omega^2 & \Lambda_{11}(1,2) \\ \Lambda_{11}(2,1) & \Lambda_{11}(1,1) - m\omega^2 \end{array} \right| & = 0 \\
 \text{b)} & \left| \begin{array}{cc} \Lambda_{22}(1,1) - m\omega^2 & \Lambda_{22}(1,2) \\ \Lambda_{22}(2,1) & \Lambda_{22}(1,1) - m\omega^2 \end{array} \right| & = 0 \\
 \text{c)} & \left| \begin{array}{cc} \Lambda_{33}(1,1) - m\omega^2 & \Lambda_{33}(1,2) \\ \Lambda_{33}(2,1) & \Lambda_{33}(1,1) - m\omega^2 \end{array} \right| & = 0
 \end{array} \quad \left. \vphantom{\begin{array}{l} \text{a)} \\ \text{b)} \\ \text{c)} \end{array}} \right\} (3.34)$$

By making use of the identity

$$\Lambda(2,1) = \Lambda^*(1,2) \quad , \quad (3.35)$$

the solution of the determinants have the form

$$m\omega^2 = \Lambda_{jj}(1,1) \pm [\Lambda_{jj}(1,2) \Lambda_{jj}^*(1,2)]^{\frac{1}{2}} \quad . \quad (3.36)$$

As the elements of the dynamical matrix $\Lambda(q)$ are functions of q , the phonon dispersion curves in the $[0001]$ direction may be found by forming the value of q parallel to the above direction.

So the conditions

$$\left. \begin{array}{l} q_3 = q \\ q_1 = q_2 = 0 \end{array} \right\} \quad (3.37)$$

are substituted into the matrix elements used in equation (3.36).

From the discussion in Chapter 2 there should be two

transverse waves and one longitudinal wave. The longitudinal wave is polarized in the direction of propagation and the frequency is given by the following equation.

$$\begin{aligned} v_L &= \left\{ \frac{1}{4\pi^2 m} [\Lambda_{33}(1,1) \pm (\Lambda_{33}(1,2) \Lambda_{33}^*(1,2))^{\frac{1}{2}}] \right\}^{\frac{1}{2}} \\ &= \left\{ \frac{1}{4\pi^2 m} [\Lambda_Z(1 \pm \cos \frac{q}{2}) + 4A^{(4)}(1 - \cos^2 \frac{q}{2})] \right\}^{\frac{1}{2}}, \quad (3.38) \end{aligned}$$

where

$$\Lambda_Z = 6B + \frac{3}{2} \left(\frac{c}{a} \right)^2 (E(2) + E(3)).$$

Because of the symmetry in the [0001] direction the two transverse waves are identically given by

$$v_T = \left\{ \frac{1}{4\pi^2 m} [\Lambda_x(1 \pm \cos \frac{q}{2}) + 4B^{(4)}(1 - \cos^2 \frac{q}{2})] \right\}^{\frac{1}{2}}, \quad (3.39)$$

where

$$\Lambda_x = 6B + E(2) + 4E(3).$$

The choice of signs in the equations enable the acoustic modes to be calculated using the negative sign and the optical modes using the positive sign. By plotting the frequency v against $q/q_{\max}$, where $q_{\max} = \pi$, the phonon relations in the [0001] direction may be found.

The expressions for the frequencies at the points $q = 0$ and $q = q_{\max}$ are useful in determining the force constants. This is because the frequencies can be experimentally determined most accurately at these points. So by using the equations involving the elastic constants and also the equations for a number of points on the phonon dispersion curves, the force constants may be found. The

equations below give the dispersion relationships at $q = 0$ and $q = q_{\max}$ in the $[0001]$ direction.

$$m\omega_t^2 (q = 0) = 2\Lambda_x \quad (3.40)$$

$$m\omega_l^2 (q = 0) = 2\Lambda_z \quad (3.41)$$

$$m\omega_t^2 (q = q_{\max}) = \Lambda_x + 4B^{(4)} \quad (3.42)$$

$$m\omega_l^2 (q = q_{\max}) = \Lambda_z + 4A^{(4)} \quad (3.43)$$

The procedure for determining the dispersion relations in the $[01\bar{1}0]$ direction is similar to that already discussed for the $[0001]$ direction. In order for q to be parallel to the $[01\bar{1}0]$ direction the following conditions are necessary.

$$\left. \begin{array}{l} q_2 = q \\ q_1 = q_3 = 0 \end{array} \right\} \quad (3.44)$$

On this occasion the longitudinal wave is given by

$$v_L = \left\{ \frac{1}{4\pi^2 m} [\Lambda_{22}(1,1) \pm (\Lambda_{22}(1,2) \Lambda_{22}^*(1,2))^{\frac{1}{2}}] \right\}^{\frac{1}{2}} \quad (3.45)$$

The transverse waves are found by putting $k = 1$ or 3 in the following expression.

$$v_T = \left\{ \frac{1}{4\pi^2 m} [\Lambda_{kk}(1,1) \pm (\Lambda_{kk}(1,2) \Lambda_{kk}^*(1,2))^{\frac{1}{2}}] \right\}^{\frac{1}{2}}, \quad (3.46)$$

where the conditions (3.44) have been applied to the matrix elements Λ_{kk} . By putting $q = q_{\max}$ in equation (3.45) and (3.46)

the following equations are obtained.

$$\text{L.O.} \quad m\omega_{22}^2 = C + 6A + 2/3 E(2) , \quad (3.47)$$

$$\text{L.A.} \quad m\omega_{22}^2 = D + 6A + 4/3 E(2) + 8E(3) , \quad (3.48)$$

$$\text{T.O.} \quad m\omega_{11}^2 = C + 2A + 2E(2) , \quad (3.49)$$

$$\text{T.A.} \quad m\omega_{11}^2 = D + 2A + 8E(3) , \quad (3.50)$$

$$\text{T.O.} \quad m\omega_{33}^2 = C + 2 \left(\frac{c}{a} \right)^2 E(2) , \quad (3.51)$$

$$\text{T.A.} \quad m\omega_{33}^2 = D + \left(\frac{c}{a} \right)^2 (E(2) + 3E(3)) , \quad (3.52)$$

where

$$C = 8(B^{(1)} + B^{(2)}) ,$$

$$A = [A^{(1)} - B^{(1)}] \text{ and } D = 4(2B^{(1)} + B^{(2)} + 3B^{(3)}) .$$

The two letters before the equations describe the wave as longitudinal (L) or transverse (T) and acoustical (A) or optical (O).

Chapter 4

4.1. Results and Discussion

The calculations were initially carried out for Magnesium, Beryllium and Zinc, using interactions out to the third nearest neighbours. This results in a particularly simple expression for the phonon dispersion relations in the [0001] direction. On substituting equation (3.27) into equation (3.39) and letting $B^{(4)} = 0$, the transverse branch is given by

$$v_T = \left(\frac{1}{4\pi^2 m} \right) \frac{2\sqrt{3}}{c} a^2 C_{44} (1 \pm \cos \pi c q) . \quad (4.1)$$

Similarly the longitudinal branch is given by

$$v_L = \left(\frac{1}{4\pi^2 m} \right) \frac{2\sqrt{3}}{c} a^2 C_{33} (1 \pm \cos \pi c q) . \quad (4.2)$$

The dispersion relations in the [01 $\bar{1}$ 0] direction are calculated by substituting values for the force constants into equations (3.45) and (3.46). The force constants were obtained by solving six linear simultaneous equations that expressed experimentally determined data. The expressions for the elastic constants C_{33} , C_{44} and C_{13} (equations 3.26, 3.27 and 3.28) together with Huang's condition for vanishing deviatoric stress (equation 3.32) were four of the equations used. Another linear equation was obtained by adding together the non linear expressions for the elastic constants C_{11} and C_{12} .

A difficulty arising from this last equation is that although the force constants may predict the correct value of $C_{11} + C_{12}$, the individually predicted values may be incorrect. The expression (equation 3.51) for the frequency of the transverse optical mode, polarized perpendicular to the basal plane on the zone boundary in the $[01\bar{1}0]$ direction, completed the set of equations.

Although the general features given by the phonon dispersion curves are in general agreement with the experimental results, with the exception of Magnesium, the detailed agreement is poor. The preliminary calculations for Beryllium showed that for this element the results were extremely sensitive to the model. In order that the chosen values of the elastic constants may predict consistent results it was necessary to introduce the following condition,

$$C_{11} - 3C_{12} \approx 2(C_{44} - C_{13}) \quad (4.3)$$

This condition is found by assuming that the non linear expression, in the equations for C_{11} and C_{12} is negligible. This assumption is justified as a check showed that the maximum discrepancy was less than 2.5%. No improvement in the results for Zinc could be found by using the condition (4.3).

The elastic constants chosen in order to deduce the force constants are compared with their corresponding experimental values in Table 4. The associated force constants are given in Table 5.

Table 4

		C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	c/a
Be	value used	2.99	0.13	0.19	3.08	1.49	1.57
	experimental value [18]	2.99	0.28	0.11	3.42	1.66	1.57
Mg	value used	0.643	0.244	0.217	0.657	0.181	1.63
	experimental value [19]	0.628	0.259	0.217	0.657	0.181	1.63
Zn	value used	1.361	0.775	0.552	0.677	0.448	1.86
	experimental value [20]	1.768	0.368	0.552	0.677	0.448	1.86

The Elastic constants are in units of 10^{12} dynes/cm².

The phonon dispersion curves obtained using the force constants from Table 5 are shown in Figures 1 and 2, where they are compared with experimental data[21,14,22,23].

Table 5

	A(1)	A(2)	A(3)	B(1)	B(2)	B(3)
Be	2.437	3.002	1.002	0.097	0.152	0.392
Mg	1.108	1.094	0.105	0.0096	0.0095	-0.0298
Zn	2.042	0.198	1.187	0.059	0.076	-0.118

The force constants are in units of 10^4 dynes/cm.

A histogram of the frequency spectrum was obtained by solving equation (2.23) for a random sample of 2500 $\mathbf{q}$ vectors in $1/24$ of the Brillouin zone and plotting the number of roots

that lie within a given frequency interval against frequency. The results are shown in Figures 3. The histogram is normalized according to equation (2.65). The results of Young and Koppel [24] are also shown in Figures 3. These authors have used a central force law with interactions out to fifth nearest neighbours for Beryllium. For Magnesium a tensor force law with interactions out to fourth nearest neighbours was used. The tensor force law which they adopted for Zinc is rather curious insofar as the interactions out to the sixth nearest neighbours are included but there is no contribution from the fourth and fifth nearest neighbours. However, the results from the present computation are in general agreement with the results of these authors. In order to improve the form of the histogram, the number of random samples of q vectors was increased to 5000. This did not significantly change the histogram, but the amount of computing time required was almost doubled.

The Specific Heats were calculated using the frequency spectrum shown in Figures 3 and the equation (2.66). For Magnesium the Specific Heat at constant volume is plotted against the temperature and compared with experimental data [25] in Figure 4. The calculated values of the specific Heats for Beryllium and Zinc were in poor agreement with the experimental values. Similarly there was poor agreement with the Debye Temperature [section 2.6] for Magnesium. This is probably because no account has been taken of the anharmonic effects present or of the electronic contribution in the determination of the force constants.

4.2. Methods of Improving the Model

It is worth discussing a number of interesting relations between the equations for the elastic constants and the frequencies on the zone boundaries in the $[0001]$ and $[01\bar{1}0]$ directions. These relations create restrictions upon the choice of experimental values to be used in conjunction with the elastic constants to determine the force constants. When considering interactions out to the third nearest neighbours the following relationships are readily obtained.

$$2 m\omega_t^2 (q = q_{\max}) = m\omega_t^2 (q = 0) . \quad (4.4)$$

$$2\sqrt{3}c C_{44} = \left(\frac{c}{a} \right)^2 m\omega_t^2 (q = q_{\max}) . \quad (4.5)$$

$$4\sqrt{3}c C_{44} = \left(\frac{c}{a} \right)^2 m\omega_t^2 (q = 0) . \quad (4.6)$$

There is a similar set of equations for the longitudinal modes and the elastic constant C_{33} . All the equations discussed here are shown between equations (3.26) to (3.30) and (3.40) to (3.43). Now the experimental values of $m\omega^2$ given in Table 6 appear to be incompatible with the above equations, except for Magnesium. However, if the interactions are considered out to fourth, fifth and sixth nearest neighbours then the following relation always exist.

Table 6

Phonon energies $m\omega^2$ ($\times 10^4$ ergs)

		$q = 0$	$q = q_{\max} [0001]$	$q = q_{\max} [01\bar{1}0]$
Be	OPTICAL $m\omega^2_{11}$	10.4	6.776	-
	$m\omega^2_{22}$	10.4	6.776	15.69
	$m\omega^2_{33}$	23.39	14.451	16.87
	ACOUSTICAL $m\omega^2_{11}$	0	6.776	-
	$m\omega^2_{22}$	0	6.776	14.006
	$m\omega^2_{33}$	0	14.451	8.65
Mg	OPTICAL $m\omega^2_{11}$	2.54	1.25	4.47
	$m\omega^2_{22}$	2.54	1.25	7.58
	$m\omega^2_{33}$	8.35	4.32	6.08
	ACOUSTICAL $m\omega^2_{11}$	0	1.25	2.18
	$m\omega^2_{22}$	0	1.25	7.04
	$m\omega^2_{33}$	0	4.32	2.81
Zn	OPTICAL $m\omega^2_{11}$	1.91	0.97	-
	$m\omega^2_{22}$	1.91	0.97	16.93
	$m\omega^2_{33}$	7.34	7.23	2.13
	ACOUSTICAL $m\omega^2_{11}$	0	0.97	-
	$m\omega^2_{22}$	0	0.97	15.26
	$m\omega^2_{33}$	0	7.23	0.98

$$4\sqrt{3}c \, C_{44} = \left(\frac{c}{a} \right)^2 (4m\omega_t^2 (q = q_{\max}) - m\omega_t^2 (q = 0)) \quad (4.7)$$

There is a similar equation for the longitudinal mode

$$4\sqrt{3}c \, C_{33} = \left(\frac{c}{a} \right)^2 (4m\omega_l^2 (q = q_{\max}) - m\omega_l^2 (q = 0)) \quad (4.8)$$

If all the equations are considered up to the fourth nearest neighbours then the discrepancy involved in equation (4.4) is found to be related to the force constant $B^{(4)}$ by the equation

$$2m\omega_t^2 (q = q_{\max}) - m\omega_t^2 (q = 0) = 8B^{(4)} \quad (4.9)$$

Similarly from the longitudinal modes the central force constant $A^{(4)}$ is given by

$$2m\omega_l^2 (q = q_{\max}) - m\omega_l^2 (q = 0) = 8A^{(4)} \quad (4.10)$$

Thus in view of the above equations it is impossible using the theoretically calculated force constants for three nearest neighbours to match the experimentally determined phonon dispersion curves and the elastic constants. It was therefore desirable to repeat the calculations for the force constants using four nearest neighbour interactions.

The extension of the model made no noticeable difference to the results of Beryllium and Zinc, although there was an improvement for Magnesium. The force constants for Magnesium, using four neighbour interactions, are given in Table 7.

Table 7

	A(1)	A(2)	A(3)	A(4)	B(1)	B(2)	B(3)	B(4)
Mg	1.133	1.055	0.0958	0.0357	0.0507	0.0196	-0.0631	0.0174

The force constants are in units of 10^4 dynes/cm

Note that Magnesium appeared to satisfy equation (4.4) because of the low values of $A^{(4)}$ and $B^{(4)}$. The elastic constants used in the calculation are given in Table 8 and the phonon dispersion curves shown in Figures 5A and 5B.

Table 8

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	c/a
Mg value used	0.644	0.242	0.217	0.657	0.181	1.63
Mg experimental value [19]	0.628	0.259	0.217	0.657	0.181	1.63

The elastic constants are in units of 10^{12} dynes/cm².

There is a further restriction on the accuracy of the force model involving interactions of both third and fourth nearest neighbours. This restriction is given by the following equation, which involves Huang's vanishing stress condition,

$$\omega_{33}^2 (\text{T.A.}) = \frac{4}{3} (\sqrt{3} c C_{44}) + \frac{1}{9} \omega_1^2 (q = 0) . \quad (4.11)$$

For Magnesium the frequency of the transverse acoustic mode, on the zone boundary in the $[01\bar{1}0]$ direction, can be calculated using equation (4.11) and found to be accurate within the allowed experimental error. However, when equation (4.11) is applied to Beryllium and Zinc an interesting complication arises. The calculated values of the acoustic modes are within the experimental errors allowed in the determination of the values of the corresponding optical modes. This would seem to suggest that there is some mixing of acoustic and optical modes.

The calculations involving the fourth nearest neighbours were carried out in order to see whether there was much of an improvement in the dispersion curves due to including equations (4.9) and (4.10). It was necessary to solve eight linear simultaneous equations to determine the force constants. Six of the equations were those previously used in the calculations for third neighbour interactions. The other two equations used with experimentally determined data were $m\omega_t^2 (q = q_{\max})$ and $m\omega_L^2 (q = q_{\max})$ (equations 3.42 and 3.43). The choice of equations used with their corresponding experimental data was limited not only by the dependent relationships already given but by the lack of experimental data for the transverse modes polarized parallel to the basal plane of Beryllium and Zinc in the $[01\bar{1}0]$ direction.

The Phonon Dispersion curves were also calculated for Magnesium using a tensor force model due to Begbie and Born [2]. This could improve the model as the only assumption made about the forces is that they are an arbitrary function of the atomic

positions. The tensor forces have previously been calculated by P.K. Iyengar et al [26] for both three and four nearest neighbours. The fourth neighbour tensor force model, used in these calculations, requires 14 atomic force constants. Two of the force constants used in evaluating the elastic constant C_{13} are not used in the determination of the phonon dispersion curves in the [0001] and [01 $\bar{1}$ 0] directions. So using the condition for lattice equilibrium only eleven independent constants are necessary to determine the dispersion relations. As there are only 4 available independent elastic constants, phonon frequencies at selected points in the Brillouin zone are used as additional data to determine the force constants.

The eleven equations used in the calculations are given below.

$$\begin{aligned}
 & \frac{\sqrt{3}}{2} c (C_{11} + C_{12}) = 12\beta - 4\mu - 16\eta \\
 & \frac{\sqrt{3}}{2} c C_{33} = \left(\frac{c}{a} \right)^2 \left\{ \frac{3}{2} (\nu + \zeta) + 2\phi \right\} \\
 & \frac{\sqrt{3}}{2} c C_{44} = \left(\frac{c}{a} \right)^2 \left\{ \frac{3}{2} (\lambda + \epsilon) + 2\theta \right\} \\
 & 3\gamma + \nu + 4\zeta = \left[\frac{3}{2} (\lambda + \epsilon) + 2\theta \right] (c/a)^2 \\
 & m\omega_L^2 [0001] (q = 0) = 12 (\nu + \zeta) \\
 & m\omega_t^2 [0001] (q = 0) = 12 (\lambda + \epsilon) \\
 & \text{L.O. } m\omega_{22}^2 [01\bar{1}0] (q = q_{\max}) = 8 (\lambda + \alpha + \beta + \mu) \\
 & \text{T.O. } m\omega_{33}^2 [01\bar{1}0] (q = q_{\max}) = 8 (\nu + \gamma) \\
 & \text{T.O. } m\omega_{11}^2 [01\bar{1}0] (q = q_{\max}) = 8 (\lambda + \alpha - \beta - \mu) \\
 & \text{L.A. } m\omega_{22}^2 [01\bar{1}0] (q = q_{\max}) = 4\lambda + 8 (\alpha + \beta - \mu) + 12\epsilon \\
 & \text{T.A. } m\omega_{33}^2 [01\bar{1}0] (q = q_{\max}) = 4\lambda + 8 (\alpha - \beta + \mu) + 12\epsilon
 \end{aligned} \tag{4.12}$$

The value of the force constants and the elastic constants follow

$$\begin{aligned}
 \phi &= 0.036 ; & \theta &= 0.017 ; \\
 \nu &= 0.708 & \gamma &= 0.052 ; \\
 \zeta &= -0.012 ; & \beta &= 0.238 ; \\
 \mu &= -0.066 ; & \lambda &= 0.236 ; \\
 \alpha &= 0.539 ; & \epsilon &= -0.054 ; \\
 \eta &= -0.055 ;
 \end{aligned}$$

The force constants are in units of 10^4 dynes/cm.

	C_{11}	C_{12}	$C_{11} + C_{12}$	C_{33}	C_{44}	c/a
calculated values	0.577	0.305	0.882	0.654	0.180	1.63
exp. values [19]	0.628	0.259	0.887	0.657	0.181	1.63

The elastic constants are in units of 10^{12} dynes/cm². In the limit of an axisymmetric force law the tensor force constants reduce to;

$$\begin{aligned}
 \alpha &= \frac{1}{2} (A^{(1)} + B^{(1)}) ; & \beta &= \frac{1}{4} (A^{(1)} - B^{(1)}) ; \\
 \gamma &= B^{(1)} ; & \delta &= 0 ; \\
 \lambda &= B^{(2)} + E(2)/6 ; & \mu &= -E(2)/12 ; \\
 \nu &= B^{(2)} + \left[\frac{c}{a} \right]^2 E(2)/4 ; & \epsilon &= B^{(2)} + 2/3 E(3) ; \\
 \eta &= -E(3)/3 ; & \zeta &= B^{(3)} + \left[\frac{c}{a} \right]^2 E(3)/4 ; \\
 \theta &= B^{(4)} ; & \phi &= A^{(4)} ;
 \end{aligned}$$

The Phonon Dispersion curves for Magnesium using the tensor force model are in good agreement with experimental data and are shown in Figures 6. It is not possible to carry out a detailed examination for Beryllium and Zinc because the

experimental values for the transverse modes in the $[01\bar{1}0]$ direction, polarized parallel to the basal plane, are not available.

4.3. Conclusion

The conclusion arrived at is that whilst simple force constant models are useful in discussing the general harmonic properties of lattices, they are not adequate for calculating the detailed phonon dispersion relations of metals.

The most satisfactory approach to the theory of the lattice dynamics of metals appears to be that of Toya [27], who used the solution of the electron-phonon problem given by Bardeen [28]. Although Toya's model is more suitable for the alkalis than for polyvalent metals Sham's [13] formulation of the problem using pseudo-potential methods offers a realistic alternative to the rather artificial force constant methods.

For a more detailed account of the pseudo-potential method applied to lattice vibrations the reader is referred to Chapter 7 of Harrison's book [14].

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References

- [1] M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Clarendon Press, Oxford, 1954.
- [2] G.H. Begbie and M. Born, Proc. Roy. Soc. (London) A188, 179 (1947).
- [3] G.H. Begbie, Proc. Roy. Soc. (London) A188, 189 (1947).
- [4] M. Born, 1923 Atomtheorie des festen Zustandes. Leipzig.
- [5] P.C. Fine, Phys. Rev. 56, 355 (1939).
- [6] R.B. Leighton, Revs. Mod. Phys. 20, 165 (1948).
- [7] Jules de Launay, Solid State Physics 2, 220 (1956).
- [8] L.J. Slutsky and C.W. Garland, J. Chem. Phys. 26, 787 (1957).
- [9] E.A. Metzbower, Phys. Stat. Sol., 20, 681 (1967).
- [10] idem, ibidem, 25, 403 (1968).
- [11] idem, Phys. Rev., 177, 1139 (1969).
- [12] L.J. Sham, Proc. Roy. Soc. A283, 33 (1965).
- [13] A.J. Pindor and R. Pynn, J. Phys. C 2, 1037 (1969).
- [14] W.A. Harrison, Pseudopotentials in the Theory of Metals, W.A. Benjamin Inc., 1966.
- [15] M.J.P. Musgrave, Crystal Acoustics, Holden-Day (1970).
- [16] E.S.R. Gopal, Specific Heats at Low Temperatures, Heywood Books (1966).
- [17] J.F. Smith and C.L. Arbogast, J. Appl. Phys., 31, 99 (1950).
- [18] L.J. Slutsky and C.W. Garland, Phys. Rev., 107, 972 (1957).
- [19] C.W. Garland and R. Dalven, Phys. Rev., 111, 1232 (1958).
- [20] K. Huang, Proc. Roy. Soc., A203, 178 (1950).

- [21] R.E. Schmunk, R.M. Brugger, P.D. Rondolph and K.A. Strong, Phys. Rev., 128, 562 (1962).
- [22] E. Maliszewski, J. Rosolowski, D. Sledziowska and A. Czachor, Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963, edited by R.F. Wallis. (Pergamon Press Inc., New York, 1965).
- [23] G. Borgonovi, G. Caglioti and J.J. Antal, Phys. Rev., 132, 683 (1963).
- [24] J.A. Young and J.U. Koppel, Phys. Rev., 134, 1476 (1964).
- [25] Craig, R.G. Krier, C.A., Coffey, L.W., Bates, E.A., Wallace, W.E., (1954) J. Amer. Chem. Soc. 76, 238.
- [26] P.K. Iyengar, G. Venkataramen, P.R. Vijayaraghavan and A.C. Roy, Inelastic Scattering of Neutrons in Solids. International Atomic Energy Agency, Vienna 1963.
- [27] T. Toya, J. Inst. Catal. Hokkaido Univ., 6 183 (1958).
- [28] J. Bardeen Phys. Rev., 52, 688 (1937).

Appendix Dynamical Matrix Elements

$$\Lambda_{11}(\underline{q}; 1,1) = G + \Lambda_x + F - A [2C_1 + (C_2 + C_{1,2})/2 - 3] \quad .$$

$$\Lambda_{22}(\underline{q}; 1,2) = G + \Lambda_x + F - \frac{3}{2} A (C_2 + C_{1,2}) - 2) \quad .$$

$$\Lambda_{33}(\underline{q}; 1,2) = G + \Lambda_z + 2A^{(4)} (1 - C_3) \quad .$$

$$\begin{aligned} \Lambda_{11}(\underline{q}; 1,2) = & -\frac{E(2)}{4} (C_2 + C_{1,2} + C_{2,3} + C_{1,2,3}) \\ & - 2 E(3) C_1 (1 + C_3) - B^{(2)} (1 + C_3 + C_{2,3} + C_2 \\ & + C_{1,2,3} + C_{1,2}) - B^{(3)} (C_{1,22} + C_{1,22,3} \\ & + 2 C_1 (1 + C_3) + i [B^{(2)} (S_3 + S_{2,3} + S_2 + S_{1,2,3} \\ & + S_{1,2}) + B^{(3)} (S_{1,22} + S_{1,22,3} + 2 C_1 S_3) \\ & + E(2)/4 (S_2 + S_{1,2} + S_{2,3} + S_{1,2,3}) + 2E(3) C_1 S_3] \quad . \end{aligned}$$

$$\begin{aligned} \Lambda_{22}(\underline{q}; 1,2) = & - B^{(2)} (1 + C_3 + C_{2,3} + C_2 + C_{1,2,3} \\ & + C_{1,2}) - E(2)/12 (4(C_3 + 1) + C_{2,3} + C_2 \\ & + C_{1,2,3} + C_{1,2}) - B^{(3)} (C_{1,22} + C_{1,22,3} \\ & + 2 C_1 (1 + C_3)) - 4E(3)/3 (C_{1,22} + C_{1,22,3} \\ & + C_1/2 (1 + C_3)) + i[B^{(2)} (S_3 + S_{2,3} + S_2 \\ & + S_{1,2,3} + S_{1,2}) + B^{(3)} (S_{1,22} + S_{1,22,3} \\ & + 2 C_1 S_3) + E(2)/12 (4 S_3 + S_{2,3} + S_2 \\ & + S_{1,2,3}) + 4E(3)/3 (S_{1,22} + S_{1,22,3} + 2 C_1 S_3)] \quad . \end{aligned}$$

$$\begin{aligned}
 \Lambda_{33}(\underline{q}; 1,2) = & -B^{(2)}(C_3 + 1 + C_{2,3} + C_2 + C_{1,2,3}) + C_{1,2}) \\
 & - B^{(3)}(C_{1,22} + C_{1,22,3} + 2C_1(1 + C_3)) - \left(\frac{c}{a}\right)^2 \frac{E^{(2)}}{4} \\
 & (1 + C_2 + C_3 + C_{1,2} + C_{2,3} + C_{1,2,3}) - \left(\frac{c}{a}\right)^2 \frac{E^{(3)}}{4} \\
 & (C_{1,22} + C_{1,22,3} + 2C_1(1 + C_3)) + i[B^{(2)}(S_3 \\
 & + S_{2,3} + S_2 + S_{1,2,3} + S_{1,2}) + B^{(3)}(S_{1,22} \\
 & + S_{1,22,3} + 2C_1 S_3) + \left(\frac{c}{a}\right)^2 \frac{E^{(2)}}{4} (S_3 + S_{2,3} \\
 & + S_2 + S_{1,2,3} + S_{1,2}) + \left(\frac{c}{a}\right)^2 \frac{E^{(3)}}{4} (S_{1,22} + S_{1,22,3} \\
 & + 2C_1 S_3)] .
 \end{aligned}$$

$$\Lambda_{12}(\underline{q}; 1,1) = \frac{\sqrt{3}}{2} A(C_2 - C_{1,2}) .$$

$$\Lambda_{13}(\underline{q}; 1,1) = \Lambda_{23}(\underline{q}; 1,1) = 0$$

$$\begin{aligned}
 \Lambda_{12}(\underline{q}; 1,2) = & \frac{\sqrt{3}}{12} E^{(2)}(C_{2,3} + C_2 - C_{1,2,3} - C_{1,2}) \\
 & - \frac{2}{3} \sqrt{3} E^{(3)} S_1 S_3 + i \left[\frac{\sqrt{3}}{12} E^{(2)} (S_{1,2,3} + S_{1,2} \right. \\
 & \left. - S_{2,3} - S_2) - \frac{2}{3} \sqrt{3} E^{(3)} S_1 (1 + C_3) \right]
 \end{aligned}$$

$$\begin{aligned}
 \Lambda_{13}(\underline{q}; 1,2) = & \frac{c}{a} \frac{E^{(2)}}{4} (-C_{2,3} + C_2 + C_{1,2,3} \\
 & - C_{1,2}) + \frac{c}{a} E^{(3)} S_1 S_3 + i \left[-\frac{c}{4a} E^{(2)} (S_{2,3} - S_2 \right. \\
 & \left. - S_{1,2,3} + S_{1,2}) + \frac{c}{a} E^{(3)} S_1 (1 - C_3) \right] .
 \end{aligned}$$

$$\begin{aligned} \Lambda_{23}(\underline{q}; 1,2) = & \frac{\sqrt{3}}{12} \frac{c}{a} E(2) (2 - 2 C_3 + C_{2,3} - C_2 + C_{1,2,3} \\ & - C_{1,2}) - \frac{\sqrt{3}}{6} \frac{c}{a} E(3) (2 C_{1,22,3} - 2 C_{1,22} \\ & + 2 C_1 (1 - C_3)) + i \left[- \frac{\sqrt{3}}{12} \frac{c}{a} E(2) (2 S_3 \right. \\ & - S_{2,3} + S_2 - S_{1,2,3} + S_{1,2}) - \frac{\sqrt{3}}{6} \frac{c}{a} E(3) \\ & \left. (2 S_{1,22} - 2 S_{1,22,3} + 2 C_1, S_3) \right] . \end{aligned}$$

where $B = B^{(2)} + B^{(3)}$, $D = 4 (2B^{(1)} + B^{(2)} + 3B^{(3)})$,

$$G = 2B^{(1)} [3 - (C_1 + C_2 + C_{1,2})] ,$$

$$F = 2B^{(4)} (1 - C_3) ,$$

$$\Lambda_x = 6B + E(2) + 4 E(3) ,$$

$$\Lambda_z = 6B + \frac{3}{2} \left(\frac{c}{a} \right)^2 (E(2) + E(3)) .$$

$$C_{j,k} = \cos (J + k) \text{ where if } j = 1,2 \text{ then}$$

$$J = \underline{q}_j a \text{ and if } j = 3 \text{ then } J = \underline{q}_3 c .$$

The first of the two subscripts following a comma denotes the multiple of the following $\underline{q}$ value.

$$\text{Thus } C_{j,kk} = \cos (\underline{q}_j a + k \underline{q}_k a) .$$

S is used similarly as an abrieviation for sin.

Figure Captions

- Fig. 1A Beryllium: The phonon dispersion relations for the [0001] direction. The calculated curves are compared with experimental data from reference [21].
- Fig. 1B Magnesium: The phonon dispersion relations for the [0001] direction. The calculated curves are compared with experimental data from reference [13].
- Fig. 1C Zinc: The phonon dispersion relations for the [0001] direction. The calculated curves are compared with two sets of experimental data, the open circles are taken from reference [22] and the closed ones from reference [23].
- Fig. 2A Beryllium: The phonon dispersion relations for the [01 $\bar{1}$ 0] direction. The calculated curves are compared with experimental data from reference [21].
- Fig. 2B Magnesium: The phonon dispersion relations for the [01 $\bar{1}$ 0] direction. The calculated curves are compared with experimental data from reference [13].
- Fig. 2C Zinc: The phonon dispersion relations for the [01 $\bar{1}$ 0] direction. The calculated curves are compared with two sets of experimental data, the open circles are taken from reference [22] and the closed ones from reference [23].
- Fig. 3A The frequency spectrum of Beryllium. The smooth curve is taken from the result of Young and Koppel [24].
- Fig. 3B The frequency spectrum of Magnesium. The smooth curve is taken from the result of Young and Koppel [24].

- Fig. 3C The frequency spectrum of Zinc. The smooth curve is taken from the result of Young and Koppel [24].
- Fig. 4 The Specific Heat at constant volume for Magnesium. The calculated curve is compared with experimental data from reference [25].
- Fig. 5A Magnesium: The phonon dispersion relations for the $[0001]$ direction in the extended model. The calculated curves are compared with experimental data from reference [13].
- Fig. 5B Magnesium: The phonon dispersion relations for the $[01\bar{1}0]$ direction in the extended model. The calculated curves are compared with experimental data from reference [13].
- Fig. 6A Magnesium: The phonon dispersion relations for the $[0001]$ direction in the tensor force model. The calculated curves are compared with experimental data from reference [13].
- Fig. 6B Magnesium: The phonon dispersion relations for the $[01\bar{1}0]$ direction in the tensor force model. The calculated curves are compared with experimental data from reference [13].

FIG. 1A

FIG. 1B

FIG. 1C

FREQUENCY (units of 10^{12} sec^{-1})

Zn [0001]

q/q_{max}

FIG. 2A

FIG. 2B

FIG. 3B

FIG. 4

C_v of Mg (in cal./deg. g. atom)

4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

TEMPERATURE (in °K)

0 20 40 60 80 100

FIG. 5A

FIG. 5B

FIG. 6A

FREQUENCY (units of 10^{12} sec^{-1})

Mg [0001]

q/q_{max}

FIG. 6B