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University Microfilms International 300 N. ZEEB ROAD, ANN ARBOR, MI 48106 Lattice dynamics of hcp and bcc zirconium

by

Jerel L. Zarestky

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

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CHAPTER I. INTRODUCTION

Properties of Zirconium

Zirconium has been and continues to be a material of considerable experimental interest due to its structural characteristics and the temperature dependence of its electrical and thermodynamic properties. Pure zirconium metal solidifies to a body centered cubic structure (β phase) at approximately 2123K (1850°C) and then undergoes a martensitic transformation to a hexagonal close-packed structure (α -phase) at approximately 1135K (862°C). (See Table 1 for basic properties of Zr.) There is also a competing structural transition to the omega (ω) phase occurring in pure zirconium under pressure (1,2) and in alloys (3-6).

Zirconium as well as other hcp transition metals (Ti and Hf) show unusual behavior in their electrical resistivity and heat capacity at constant pressure. The electrical resistivity of Zr (7) (Figure 1) above room temperature increases linearly with temperature; the normal behavior for a metal, but then saturates to a nearly constant value at about 1000K. The heat capacity (8-11) (Figure 2) increases almost linearly with temperature and even for $T/@_D >> 1$ ($@_D \sim 270-290$ K) there is no tendency for C_p to level off in accordance with the classic Dulong-Petit law at $3k_BN$ (5.96 cal/mole deg). There is also a large decrease with increasing temperature of the elastic constants (12) C_{44} and especially C_{66} which decreases by about 75% from 4K to the transition temperature (see Table 1). Studies of the temperature dependence of the normal vibrational modes, the phonon dispersion curves, provide





Figure 2. Specific heat at constant pressure of hcp Zr obtained by various workers (8-11)

Atomic mass 91.22 amu 40 Ζ bcc to hcp transition temperature (12) 1135K Lattice parameters (13) a = 3.232 Åc = 5.147 Å α Zr (hcp) at 298K $\gamma = c/a = 1.593$ a = 3.616 Å β Zr (bcc) at 1252K Thermal neutron cross section (14) 4.9 barns (10^{-24} cm^2) Coherent 1.4 barns Incoherent Absorbtion 0.1 barns Coherent neutron scattering amplitude (15) $b = 0.71 \times 10^{-12} \text{ cm}$ Elastic constants (12) (10¹³ dynes/cm²) 1007K 4K 295K 1133K 15.54 14.34 11.14 10.64 C₁₁ C_{12}^{--} 6.72 7.28 8.32 8.40 6.56 6.46 6.56 C₁₃ 6.53 C_{44} 3.63 3.20 2.28 2.01 16.48 14.14 C33 17.25 13.74 $(C_{66} = \frac{1}{2}(C_{11}-C_{12}))$ Superconducting transition temperature (13)

Table 1. Physical properties of zirconium

10 - 0.55%

Tc = 0.55K

a great deal of information useful in the understanding of the temperature dependence of the above properties.

Zirconium is also a superconductor ($T_{c} \cong 0.5K$). The superconducting transition elements have also been studied extensively using inelastic neutron scattering techniques. These studies have revealed anomalies in the phonon dispersion curves which are usually attributed to strong electron-phonon interaction (16) and are therefore related to the superconducting properties of the materials. The transition metals of the fifth and sixth columns of the periodic table (bcc in structure) have all been studied but the high temperature bcc phases of the fourth column transition elements have not because of difficulty in growing single crystals under experimental conditions.

Classical Theory of Lattice Dynamics

Crystal potential energy Φ

The presence of the weakly bound conduction electrons is the characteristic feature of the metallic crystal. It is these electrons (4d in the case of Zr) which give rise to the large electrical conductivity and aid in the binding of the ion cores. But the transition metals have a relatively high binding energy which implies there may be additional binding from the inner electron shells in the form of a van der Waals interaction and from covalent binding. This complicated nature of binding in metals makes it difficult to visualize ϕ . One method of visualization is to consider ϕ as a superposition of atomic pair potentials V(r) which are explained as follows (17). Consider an

impurity charge Ze in an electron gas.¹ The electronic charge distribution is distorted around the charge Ze, the distortion denoted by $Z^{el}(r)$. The dielectric properties of the electron gas determine the form of $Z^{el}(r)$ and in addition, $\int_R Z^{el}(r) d\vec{r} = -Z$, where R is a limited region about the impurity Ze. Therefore Ze + $Z^{el}(r)$ appears as a neutral object from a distance. A test charge (another Ze) then sees not only the impurity but the induced screening charge $Z^{el}(r)$ as well. The effective potential $\Phi(r)$ is then the interaction between the two charges Ze altered by the screening charge.

Born-von Kármán treatment of lattice dynamics

In the former section the crystal potential energy Φ was discussed in terms of electronic motion rather than nuclear motion which is the phenomenon we wish to analyze. The relationship between dynamics and binding was first justified in the case of molecular vibrations by Born and Huang (18). Their arguments, easily applied to crystals, validate the use of a potential function Φ in describing dynamics provided one assumes what is called the adiabatic approximation. In this approximation, it is assumed that since the frequency of motion of the electrons is much higher than the vibrational frequencies (by a factor of the order of $(m_i/m_e)^{\frac{1}{2}} \cong 100$), the electrons follow the nuclear motion "adiabatically". That is the electrons do not undergo

¹The term 'electron gas' used here refers to a gas of electrons with a uniform background of positive charge.

transitions from one state to another but instead the electronic states are deformed progressively as the nuclear displacements change.

Using the "adiabatic approximation" together with a perturbation procedure leads to an effective Hamiltonian for the ions with an effective ionic potential containing the electronic energy explicitly. In crystal types where there exists a large band gap between electronic ground states and excited states such as ionic crystals, the procedure is justified, but in metals where the ground states form effectively a continuum the perturbation procedure is not valid and the nuclear and electronic motions will be coupled. Arguments have been given, however, to justify the use of the adiabatic approximation for metals by Chester (19) and Ziman (20). In these treatments a general Hamiltonian for the ion-electron system is assumed of the form

$$H = \sum_{\ell} p_{\ell}^{2} / 2m_{\ell} + V_{ii}(R) + \sum_{j} p_{j}^{2} / 2m + \sum_{j>i} \frac{e^{2}}{|\vec{r}_{j} - \vec{r}_{i}|} + V_{ie}(\vec{r}, \vec{R})$$
(1.1)

where successive terms are the kinetic energy of the ions (in the case of non-Bravais lattices such as in the hcp structure, l signifies a double indexing l and h), the bare ion-ion interaction, the kinetic energy of the electrons, the electron-electron interaction and the electron ion interaction. The coordinates \vec{r} and \vec{R} are those of the electrons and ions respectively.

First, using the electronic Hamiltonian H_e , one solves the Schrödinger equation for the electronic energies $E_k(\vec{R})$ and wave

functions $\Psi_{k}(\vec{r},\vec{R})$. Notice that the electron energy depends on \vec{R} , the ionic coordinates which are fixed parameters at this point. Then the total wave function, the solution to the total Hamiltonian, is expanded in terms of the complete set $\Psi_{k}(\vec{r},\vec{R})$. The coefficients in this expansion $\Phi_{q,k}(\vec{R})$ are shown to satisfy the following equation

$$\left\{\sum_{\ell} p_{\ell}^{2} / 2m_{\ell} + V_{ii}(\vec{R}) + E_{k}(\vec{R})\right\} \Phi_{q,k}(\vec{R}) = \mathcal{E}_{q} \Phi_{q,k}(\vec{R}) , \qquad (1.2)$$

where the \mathcal{E}_{q} 's are the energy eigenvalues of the total wave equation, obtained by neglecting terms which are small in comparison with H and $E_{k}(\vec{R})$. This approximation is essentially the adiabatic approximation in this context and the resulting Equation (1.2) can be used satisfactorily for calculating the phonon energy spectra or dispersion relations. In fact Equation (1.2) can be further simplified by writing it in the form

$$\left\{\sum_{\ell} p_{\ell}^{2}/2m + \Phi(\vec{R}_{\ell})\right\} \Phi_{q} = \mathcal{E}_{q} \Phi_{q}$$
(1.3)

where the total effective potential $\Phi(\vec{R}_{l}) = V_{ii} + E_{k}$ is dependent only on the instantaneous ion coordinates.

Harmonic approximation

At this point the discussion of the lattice dynamics of metals becomes phenomenological in nature but still extremely useful. The results of this approach together with the phonon dispersion curves measured by inelastic neutron scattering enable predictions of macroscopic physical properties. The basis for this treatment is the Hamiltonian of Equation (1.3)

$$H = \sum_{\ell k} p_{\ell k}^{2} / 2m_{k} + \Phi(\vec{R}(\ell k))$$
(1.4)

where the indices l and k are for the lth cell and the kth atom in the cell. We can write $\vec{R}(lk)$ in the form

$$\vec{R}(\ell k) = \vec{X}(\ell k) + \vec{u}(\ell k)$$
 (1.5a)

$$\vec{x}(lk) = \vec{x}(l) + \vec{x}(k)$$
(1.5b)

$$\vec{x}(l) = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3$$
 (1.5c)

where $\vec{x}(lk)$ is the equilibrium position of the atom denoted by (lk), $\vec{u}(lk)$ is the displacement from the equilibrium position, $\vec{x}(l)$ is the position of the lth cell, $\vec{x}(k)$ is the position of the kth atom in this cell, the $\vec{a_i}$'s are primitive translation vectors and the l_i 's are integers. We can then write the kinetic energy term in the Hamiltonian (1.4) as

$$\sum_{\ell k} p_{\ell k}^{2} / 2mx = \frac{1}{2} \sum_{\ell k \alpha} m_{k} \dot{u}_{i}^{2} (\ell k)$$
(1.6)

where the index α denotes the cartesian component. In most cases of practical interest where we expect the $|\vec{u}(lk)|$ to be much smaller than the lattice spacing we can expand Φ in a power series of the $\vec{u}(lk)$.

$$\Phi(\vec{R}(\ell k)) = \Phi_0 + \Phi_1 + \Phi_2 + \dots$$
 (1.7a)

where

$$\Phi_{0} = \phi(\vec{R}(\ell k)) \Big|_{\vec{u}(\ell k)=0} = \Phi(\vec{x}(\ell k))$$
(1.7b)

$$\Phi_{1} = \sum_{\substack{\ell \in I \\ \ell \in I}} \Phi_{i}(\ell k) u_{i}(\ell k) = \sum_{\substack{\ell \in I \\ \ell \in I}} \frac{\partial \Phi(\vec{R}(\ell k))}{\partial u_{i}(\ell k)} \Big| u_{i}(\ell k)$$
(1.7c)
$$\Phi_{2} = \frac{1}{2} \sum_{\substack{\ell \in I \\ \ell' \in I j}} \Phi_{ij}(\ell k, \ell' k') u_{i}(\ell k) u_{j}(\ell' k') = \frac{1}{2} \sum_{\substack{\ell \in I \\ \ell' \in I j}} \left[\frac{\partial^{2} \Phi(\vec{R}(\ell k))}{\partial u_{i}(\ell k) \partial u_{j}(\ell' k')} \right] \Big| u_{i}(\ell k) u_{j}(\ell' k') .$$
(1.7d)
$$\frac{1}{2} \sum_{\substack{\ell \in I \\ \ell' \in I j}} \left[\frac{\partial^{2} \Phi(\vec{R}(\ell k))}{\partial u_{i}(\ell k) \partial u_{j}(\ell' k')} \right] \Big| u_{i}(\ell k) u_{j}(\ell' k') .$$
(1.7d)
$$\frac{1}{2} \sum_{\substack{\ell \in I \\ \ell' \in I j}} \left[\frac{\partial^{2} \Phi(\vec{R}(\ell k))}{\partial u_{i}(\ell k) \partial u_{j}(\ell' k')} \right] \Big| u_{i}(\ell k) u_{j}(\ell' k') .$$
(1.7d)

In the harmonic approximation the power series expansion is limited to the second-order term which leads to harmonic vibration of the atoms and hence the term harmonic approximation.

The first term in the expansion Φ_0 is merely a constant and therefore does not enter into the equations of motion as will be seen later. The second term Φ_1 vanishes since the $\Phi_1(lk)$ are the forces on the atom which must be zero for all lk in the equilibrium configuration. Thus the potential energy in the harmonic approximation becomes

$$\Phi = \Phi(\vec{R}(\ell k)) = \Phi_0 + \frac{1}{2} \sum_{\substack{\ell k i \\ \ell' k j}} \Phi_{ij}(\ell k, \ell' k') u_i(\ell k) u_j(\ell k) . \quad (1.8)$$

It should be mentioned at this point that in the study of the temperature dependence of the lattice dynamics of hcp zirconium anharmonic effects are critically important but they need not be considered until the thermodynamic analysis of the data is discussed. The Hamiltonian (1.4) can now be written

$$H = \frac{1}{2} \sum_{\substack{k \in i}} m_{k} \dot{u}_{i}^{2}(\ell k) + \Phi_{0} + \frac{1}{2} \sum_{\substack{k \in i\\\ell' k' j}} \Phi_{ij}(\ell k, \ell' k') u_{i}(\ell k) u_{j}(\ell k)$$
(1.9)

and using Hamilton's Equation

$$\dot{\mathbf{p}}_{i} = -\frac{\partial H}{\partial q_{i}} \tag{1.10}$$

where p_i corresponds to $m_k u_k(lk)$ and q_i corresponds to $u_i(lk)$ the equations of motion are obtained

$$-m_{k} \ddot{u}_{i}(\ell k) = \sum_{\ell' k' j} \Phi_{ij}(\ell k, \ell' k') u_{j}(\ell' k') \quad i = x, y, z \quad . \quad (1.11)$$

$$k = 1, \ldots n$$

$$\ell \neq \text{entire crystal}$$

The equations of motion are independent of Φ_0 . The Φ_{ij} can be interpreted as (interatomic) force constants (AFC's) since $\Phi_{ij}(\ell k, \ell' k')$ is the component of a force exerted on the atom at (ℓk) in the i direction when the atom at ($\ell' k'$) is displaced in the j direction.

Properties of AFC's

<u>Permutation</u> symmetry Since the order of differentiation of $\Phi(\vec{R}(lk))$ is unimportant, assuming Φ is a well-behaved function

$$\phi_{jj}(\ell k, \ell' k') = \phi_{jj}(\ell' k', \ell k) \quad . \tag{1.12}$$

<u>Translational sum rule</u> If all atoms of the crystal are translated by \vec{t} (an infinitesimal) from their equilibrium position the crystal as a whole is translated by $\vec{u}(\ell k) = \vec{t}$ with no change in individual restoring forces. From Equation (1.11) one obtains

$$0 = \sum_{\substack{\ell'k' j}} \Phi_{ij}(\ell k, \ell'k') t_{j}, \qquad (1.13a)$$

but the t_i are independent therefore

$$0 = \sum_{\substack{k' \\ k'}} \Phi_{ij}(lk, l'k') \qquad \text{for all } j \qquad (1.13b)$$

or

$$\Phi_{ij}(\ell k, \ell k) = -\sum_{\substack{\ell' k' \\ \ell' \neq \ell \\ k' \neq k}} \Phi_{ij}(\ell k, \ell' k') . \qquad (1.13c)$$

This "self force constant" $\Phi_{ij}(k, k'k')$ is merely the opposite of the sum of the force constants between atom (k) and every other atom in the lattice.

<u>Rotational sum rule</u> If the whole crystal undergoes an infinitesimal rotation, again there will be no restoring forces. The components of this rotation can be represented by a $\vec{u}(lk)$ as follows

$$u_{j}(\ell k) = \left[\vec{\Theta} \times \vec{\lambda} \ell' k'\right]_{j}$$
$$= \sum_{mn} \varepsilon_{jmn} \theta_{m} \times_{n}(\ell' k')$$
(1.14)

where \vec{a} is along the axis of rotation and ϵ_{ijk} is the Levi-Civita symbol. Putting this into the equations of motion (1.11) yields

$$0 = \sum_{\substack{\ell \in \mathcal{L}, \ell \in \mathcal$$

Again the $\boldsymbol{\theta}_m$'s are independent and

$$0 = \sum_{\substack{\ell'k' \\ j \\ n}} \Phi_{ij}(\ell k, \ell'k') \varepsilon_{jmn} x_n(\ell'k') \quad \text{for all i and } m \quad (1.16)$$

<u>Crystal symmetry</u> Crystal symmetry imposes important restrictions on the AFC's. The symmetry posessed by a crystal is demonstrated in terms of the space group (G) which is the set of operations (elements) which when applied to the crystal bring it back onto itself. The operations, denoted by X_m , are a combination of a rotation S (proper, a pure notation, or improper, a pure rotation followed by an inversion or reflection), a primitive lattice translation $\vec{x}(m)$ and in some cases a nonprimitive translation $\vec{V}(S)$. The space group for the bcc lattice does not have a $\vec{V}(S)$ and is termed symmorphic while the hcp lattice space group has an essential $\vec{V}(S)$ and is called a nonsymmorphic space group. The total operation X_m is then written in the Seitz notation as $X_m = \{S|\vec{x}(m) + \vec{V}(S)\}$ and X_m acting on the static crystal is defined

$$X_{m} \overrightarrow{x}(lk) = \overrightarrow{x}'(lk) = S \overrightarrow{x}(lk) + \overrightarrow{x}(m) + \overrightarrow{V}(S) = \overrightarrow{x}(LK) \quad . \quad (1.17)$$

The operation acting on the excited crystal is then

$$X_{m}(\vec{x}(lk) + \vec{u}(lk)) = S \vec{x}(lk) + S \vec{u}(lk) + \vec{x}(m) + \vec{V}(S) \qquad (1.18)$$
$$= \vec{x}(LK) + S \vec{u}(lk) \quad .$$

Thus after applying X_m the displacement $\vec{u'}(LK)$ of the atom at site (LK) is $S \ \vec{u} \begin{pmatrix} k \\ k \end{pmatrix}$. If we now perform the same operation X_m on another site (l'k') which becomes rotated and translated by X_m to site (L'K'), the potential of the (lk)(l'k') pair must be the same as that of the (LK)(L'K') pair, thus

$$\sum_{ij} \Phi_{ij}(\ell k, \ell' k') u_i(\ell k) u_j(\ell' k') = \sum_{mn} \Phi_{mn}(LK, L'K') u_m'(LK) u_n'(L'K')$$
$$= \sum_{mn} \Phi_{mn}(LK, L'K') S_{mp} u_p(\ell k) S_{nq} u_q(\ell' k')$$

(The S_{mp} are the elements of the 3 x 3 matrix representing S.) = $\int \Phi (LK_{L}K')S_{M}(\ell k)S_{M}(\ell k)$

$$= \sum_{ij} \left[\sum_{mn} S_{mi} \Phi_{mn} (LK, L'K') S_{nj} \right] u_{i}(\ell k) u_{p}(\ell'k')$$

$$= \sum_{ij} \left[\sum_{mn} S_{mi} \Phi_{mn} (LK, L'K') S_{nj} \right] u_{i}(\ell k) u_{p}(\ell'k')$$

$$(1.19a)$$

Thus

$$\Phi_{ij}(\ell k, \ell' k') = \sum_{mn} S_{mi} \Phi_{mn}(LK, L'K') S_{nj}$$
(1.19b)

which in matrix notation is

$$\Phi(\ell k, \ell' k') = S \Phi(LK, L'K')S \qquad (1.20a)$$

and since S represents a rotation it is orthogonal ($\tilde{S} = S^{-1}$),¹

$$\Phi(LK,L'K') = S \Phi(lk,l'k')S$$
 (1.20b)

It is this relation which will be used to determine the form of the force constant matrix. In other words it can be used to indicate vanishing elements and relations between nonvanishing elements. This is done for the bcc and hcp force constants in Appendix D. There are also some special cases for this equation which give an indication of

¹The transpose of S is denoted \tilde{S} and the inverse S^{-1} .

the form of the force constant matrices. One of these cases is for transitional symmetry where $X_m = E_m = \{1_3 | \dot{x}(m)\}$ and

٠

$$1_{3} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Then

$$\Phi_{ij}(\ell k, \ell' k') = \Phi_{ij}(\ell + mk, \ell' + mk')$$
(1.21a)

and in particular

$$\Phi_{ij}(\ell k, \ell' k') = \Phi_{ij}(0k, \ell' - \ell k') \qquad (1.21b)$$

Using Equation (1.21b) in (1.13b) gives

$$0 = \sum_{\substack{k'k'}} \Phi_{ij}(0k, l'-lk')$$
(1.22)

which is used to determine the "self force constants" $\Phi_{ij}(0k,0k)$. If the inversion operation is an element of the space group of the crystal, the crystal is called "centro-symmetric" and if the inversion leaves every atom in its same relative position in the cell (this is the case for the bcc lattice) then (17)

$$\Phi(0k, l'-lk') = \Phi(0k, l'-lK')$$
 (1.23)

If the inversion interchanges like atoms in different sublattices, that is the atom changes relative position within the cell as well as changing cell then (17)

$$\Phi(0k, l'-lk') = \Phi(l'-lk', 0k) \qquad (1.24)$$

Solutions of the equations of motion - dynamical matrix

The periodic nature of the crystal suggests solutions to the equations of motion (1.11) of the form

$$u_{j}(\ell k) = \frac{1}{\sqrt{m_{k}}} u_{i}(k|\vec{q}) \exp(i[\vec{q}\cdot\vec{x}(\ell) - \omega(\vec{q})t])$$
(1.25)

where \vec{q} is the wave vector and $\omega(\vec{q})$ is the angular frequency associated with the wave. It is understood that when the final solution is formed from a superposition of these wavelike solutions (1.25) the displacements must be real. Substituting the $u_j(kk)$ of Equation (1.25) into the equation of motion (1.11) gives

$$\exp i(\vec{q}\cdot\vec{x}(\ell))m_{k}\frac{\omega^{2}(\vec{q})}{\sqrt{m_{k}}}u_{i}(k|\vec{q}) = \sum_{\ell'k'j} \Phi_{ij}(\ell k,\ell'k)\frac{1}{\sqrt{m_{k}}}u_{j}(k'|\vec{q})$$
$$\times \exp i(\vec{q}\cdot\vec{x}(\ell')) \qquad (1.26a)$$

or

$$\omega^{2}(\vec{q})u_{i}(k|\vec{q}) = \sum_{k'j} D_{ij}(kk'|\vec{q})u_{j}(k'|\vec{q}) \qquad (1.26b)$$

where the elements of the "dynamical matrix" $D_{ij}(k,k'|\vec{q})$ are given by

$$D_{ij}(kk'|\vec{q}) = \sum_{\ell'} \frac{1}{\sqrt{m_k m_{k'}}} \Phi_{ij}(\ell k, \ell' k') \exp i(\vec{q} \cdot \vec{x}(\ell') - \vec{x}(\ell))$$
$$= \sum_{\ell'=(\ell'-\ell)} \frac{1}{\sqrt{m_k m_{k'}}} \Phi_{ij}(0k, \vec{\ell}k') \exp i(\vec{q} \cdot \vec{x}(\vec{\ell})) \qquad (1.27)$$

by using the results of translational invariance (1.21b). Equation

(1.26b) can be expressed in matrix form as

$$\omega^{2}(\vec{q}) \ \vec{u}(\vec{q}) = \underline{D}(\vec{q}) \ \vec{u}(\vec{q})$$
(1.28)

where $\vec{u}(\vec{q})$ is a 3n component vector;

$$\vec{u}(\vec{q}) = \begin{pmatrix} u_{x}(1,\vec{q}) \\ u_{y}(1,\vec{q}) \\ u_{z}(1,\vec{q}) \\ \vdots \\ \vdots \\ u_{x}(n,\vec{q}) \\ u_{y}(n,\vec{q}) \\ u_{z}(n,\vec{q}) \end{pmatrix}$$
(1.29)

and $D(\overrightarrow{q})$ is a 3n x 3n matrix;

$$\underline{D}(\vec{q}) = \begin{pmatrix} \underline{D}(11,\vec{q}) & \underline{D}(12,\vec{q}) & \dots & \underline{D}(1n,\vec{q}) \\ \underline{D}(21,\vec{q}) & \ddots & \ddots & \ddots \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \underline{D}(n,1\vec{q}) & \ddots & \ddots & \underline{D}(nn,\vec{q}) \end{pmatrix}$$
(1.30)

with $D(kk' | \vec{q})$ a 3 x 3 matrix;

$$\underline{D}(kk'|\vec{q}) = \begin{pmatrix} D_{xx}(kk'|\vec{q}) & D_{xy}(kk'|\vec{q}) & D_{xz}(kk'|\vec{q}) \\ D_{yx}(kk'|\vec{q}) & D_{yy}(kk'|\vec{q}) & D_{yz}(kk'|\vec{q}) \\ D_{zx}(kk'|\vec{q}) & D_{zy}(kk'|\vec{q}) & D_{zz}(kk'|\vec{q}) \end{pmatrix} . \quad (1.31)$$

The problem has evolved into eigenvalue problem (1.28) with 3n eigenvalues, or eigenfrequencies, $\omega_{\xi}(\vec{q})$ and eigenvectors $\vec{u}(k|\vec{q},\xi)$. This

means that we must solve the secular or characteristic equation

$$\left|\underline{D}(\vec{q}) - \omega^2(\vec{q})\underline{I}(3n)\right| = 0 \tag{1.32}$$

to obtain the 3n eigenfrequencies and eigenvectors all of which need not be distinct. As is shown in Appendix C, the symmetry of the crystal involved may dictate degeneracies in $\omega_{\xi}(\vec{q})$ at particular points \vec{q} or along an entire line for \vec{q} in a particular direction.

The dynamical matrix exhibits certain properties of importance which are manifestations of the force constant matrices and therefore the crystal symmetry. From the permutation symmetry expression (1.12) and the expression of translational symmetry (1.21b), it can be shown that

$$D_{ij}(kk'|\vec{q}) = D_{ji}^{*}(k'k|\vec{q})$$
(1.33a)

or

$$\underline{\mathbf{D}}^{\dagger}(\vec{\mathbf{q}}) = \underline{\mathbf{D}}(\vec{\mathbf{q}}) \tag{1.33b}$$

which means that $\underline{D}(\vec{q})$ is Hermitian and therefore its eigenvalues are real. It can also be shown from Equation (1.27) that

$$D_{ij}^{\dagger}(kk'|-\vec{q}) = D_{ij}(kk'|\vec{q}) \qquad (1.34a)$$

or

$$\underline{D}^{*}(-\vec{q}) = \underline{D}(\vec{q})$$
 . (1.34b)

Using the fact that $\vec{\tau} \cdot \vec{x}(\ell) = 2\pi n$, n = 0, 1, 2, ... for $\vec{\tau}$ a reciprocal lattice vector (see Appendix A), then

$$\underline{D}(\vec{q} + \vec{\tau}) = \underline{D}(\vec{q}) \quad . \tag{1.35}$$

This means that $\underline{D}(\vec{q})$ has the periodicity of the reciprocal lattice. Also, $\underline{D}(\vec{q})$ is real for $\vec{q} = 0$, $\vec{\tau}/2$ which means the dynamical matrix is real at the zone center and zone boundary.

The eigenfrequencies and eigenvectors also exhibit important properties. As was mentioned earlier $\underline{D}(\vec{q})$ is Hermitian which implies that the $\omega_{\xi}^2(\vec{q})$ are real. From the corresponding properties of $\underline{D}(\vec{q})$ one obtains

$$\omega_{\xi}^{2}(\vec{q}) = \omega_{\xi}^{2}(\vec{q} + \vec{\tau})$$
(1.36a)

and

$$\omega_{\xi}^{2}(\vec{q}) = \omega_{\xi}^{2}(-\vec{q}) \quad . \tag{1.36b}$$

The eigenvectors $\vec{u}(k|\vec{q},j)$ are usually written in the form

$$\vec{u}(k|\vec{q},\xi) = A(\vec{q},\xi)\vec{\epsilon}(k|\vec{q},\xi)$$
 (1.37)

where $A(\vec{q},\xi)$ is independent of k and time and has the same dimensions as $\vec{u}(k|\vec{q},\xi)$. The factor $\vec{\epsilon}(k|\vec{q}\cdot\xi)$ is then a unitless eigenvector of $\underline{D}(\vec{q})$ on which the orthonormality condition is imposed as

$$\vec{\epsilon}^{\dagger}(\vec{q},\xi)\vec{\epsilon}(\vec{q},\xi') = \delta_{\xi\xi'} \qquad (1.38)$$

The left side of Equation (1.38) is simply the 3n dimensional dot product (the symbol † is the vector analogy to the Hermitian adjoint operation for matrices which implies transposition followed by complex conjugation) and if expressed explicitly becomes

$$\sum_{ik} \varepsilon_i^*(k|\vec{q},\xi)\varepsilon_i(k|\vec{q},\xi') = \delta_{\xi\xi'} \qquad (1.39)$$

The set of eigenvectors also form a complete set, a condition which is expressed by the following relation

$$\sum_{\xi} \varepsilon_{i}^{*}(k|\vec{q},\xi)\varepsilon_{j}(k'|\vec{q},\xi) = \delta_{ij}\delta_{kk'} \qquad (1.40)$$

The eigenvectors again exhibit the same properties as the eigenvalues and the dynamical matrix, i.e.,

$$\vec{\epsilon}(\vec{q},\xi) = \vec{\epsilon}(\vec{q}+\vec{\tau},\xi)$$
 (1.41a)

and

$$\vec{\epsilon}(\vec{q},\xi) = \vec{\epsilon}(-\vec{q},\xi)$$
 . (1.41b)

Lattice Dynamics of a bcc Crystal

We now discuss the dynamical matrix and equations of motion specifically for the bcc lattice. Equations (1.26) and (1.27) become

$$m \omega^{2}(\vec{q}) u_{i}(\vec{q}) = \sum_{j} D_{ij}(\vec{q}) u_{j}(\vec{q}) \qquad (1.42a)$$

and

$$D_{ij}(\vec{q}) = \sum_{\underline{l}} \Phi_{ij}(\underline{l}) \exp\{i(\vec{q}\cdot\vec{x}(\underline{l}))\}$$
(1.42b)

respectively with $D_{ij}(\vec{q}) = m D_{ij}(kk | \vec{q})$ (k=k' with one atom per unit cell). Using the translational symmetry condition Equation (1.22)

$$0 = \sum_{\ell'k'} \Phi_{ij}(0k,\ell'-\ell,k') = \sum_{\overline{\ell}} \Phi_{ij}(\overline{\ell})$$
(1.43)

we can rewrite $D_{ij}(\vec{q}) = \Phi_{ij}(0) + \sum_{\overline{k} \neq 0} \Phi_{ij}(\overline{k}) \exp\{i(\vec{q} \cdot \vec{x}(\overline{k}))\}$ $= -\sum_{\overline{k} \neq 0} \Phi_{ij}(\overline{k}) [1 - \cos(\vec{q} \cdot \vec{x}(\overline{k}))] \qquad (1.44)$

Also used was the fact that the inversion operation $\{1|0\}$ is an element of the space group of the bcc lattice (this is the case for all Bravais lattices) and that

$$\Phi(\overline{k}) = \Phi(-\overline{k}) \quad . \tag{1.45}$$

We now set about simplifying $D_{ij}(\vec{q})$ and thus the equations of motion for \vec{q} along one of the symmetry directions [001], [110] or [111]. For each of these directions [hkl] there is a series of {hkl} planes perpendicular to it. For all atoms in each of these planes, $\vec{q} \cdot \vec{x}(\vec{l})$ (= $\vec{q} \cdot \vec{x}(l)$ if the reference atom is at $\vec{x}(l') = 0$) has the same value

$$\vec{q} \cdot \vec{x}(\ell') = |\vec{q}|_{hk\ell}$$
(1.46)

where $d_{hk\ell}$ is the spacing between the {hk\ell} planes. From Equation (A.4)

$$d_{hk\ell} = \frac{2\pi}{\left|\vec{\tau}_{hk\ell}\right|}$$
(1.47)

where $\vec{\tau}_{hkl}$ is the nearest reciprocal lattice point to the origin along \vec{q} . We define the reduced wave vector $\vec{\zeta}$ by

$$\vec{q} = \frac{2\pi}{a} \vec{\zeta}$$
(1.48)

and $\vec{\zeta}_m$ as the reduced wave vector at the zone boundary

$$\vec{q}_{m} = \frac{2\pi}{a} \vec{\zeta}_{m} = \frac{\vec{\tau}_{hkl}}{2} . \qquad (1.49)$$

Then

$$\vec{q} \cdot \vec{x}(\ell') = \frac{2\pi}{a} |\vec{\zeta}| \frac{\pi}{|\vec{\tau}_{hk\ell}|} = \frac{\pi |\vec{\zeta}|}{|\varsigma_m|} = \frac{\pi \zeta}{\varsigma_m}, \qquad (1.50)$$

and for the nth (hkl) plane

$$\vec{q} \cdot \vec{x}(\ell') = \frac{n\pi\zeta}{\zeta_m} . \qquad (1.51)$$

Using Equation (1.51) in Equation (1.44)

$$D_{ij}(\vec{q}) = -\sum_{n} \Phi_{n}^{i}(\xi) [1 - \cos \frac{n\pi\zeta}{\zeta_{n}}]$$
(1.52)

where $\Phi'_n(\xi)$ is the sum of all $\Phi_{ij}(\ell)$ for ℓ such that the atom at $\vec{x}(\ell)$ is in the nth plane in the $\pm[hk\ell]$ directions from the reference atom at the origin. Also, the sum in Equation (1.52) is now over pairs of planes $\pm(hk\ell)$.

The equation of motion (1.41) becomes for the mode ξ

$$m \omega_{\xi}^{2}(\vec{q}) = \sum_{n} \Phi_{n}(\xi) [1 - \cos \frac{n\pi\zeta}{\zeta_{n}}] \qquad (1.53)$$

where the $\Phi_n(\xi)$'s are the interplanar force constants and are equal to $-\Phi_n^i(\xi)$'s of Equation (1.52). We have used here the fact that along the symmetry directions the dynamical matrix factors and the $\omega_{\xi}^2(\vec{q})$'s are just linear combinations of the dynamical matrix elements (see Appendix C). The composition of the $\Phi_n(\xi)$'s in terms of the AFC's for the vibrational modes in the symmetry directions of a bcc crystal are given in Table 2 (21). For example $1^{(T[00\zeta])}$, the interplanar force constant between the (001) plane through the origin and the first two (001) planes on either side of it in the [001] direction for a T[00 ζ] mode is

$$T[00\zeta] = 8(1xx) + 8(4xx) + 8(4yy) + 8(7xx)$$

considering eight neighbors. The method for obtaining the coefficients for the AFC decomposition of the interplanar force constants is described in Appendix D.

As the wave vector for a phonon mode, \vec{q} , tends to zero, the long wavelength limit, the lattice vibrations become the acoustic vibrations of the crystal. That is for large enough λ the crystal appears to be a continuous medium. The velocity of an acoustic vibration is given by

$$V_{\xi}^{2} = C_{\xi} / \rho = \omega_{\xi}^{2}(\vec{q}) / q^{2}$$
 (1.54)

where C_{ξ} is the elastic constant or combination of elastic constants associated with the mode ξ , ρ is the density of the crystal. The C_{ξ} for a cubic crystal are given in Table 3. Solving Equation (1.54) for $\omega_{F}^{2}(\vec{q})$ one obtains

$$\omega_{\xi}^{2}(q) = \frac{q^{2}C_{\xi}}{\rho} = \frac{C_{\xi}^{4}\pi^{2}\varsigma^{2}}{\rho a^{2}} \qquad (1.55)$$

The density of a bcc crystal is

$$\rho = 2m/a^3$$
 (1.56)

since there are two atoms in the cubic unit cell. Equating the two

			-						
		(111)	(200)	(220)	(311)	(222)	(400)	(331)	(420)
	Φ _n (ξ)	α _] β _] xx xy	α ₂ β ₂ xx yy	$\alpha_3 \beta_3 \gamma_3$ xx zz xy	^α μ ^β μ ^γ μ ^δ μ xx yy yz xz	^α 5 ^β 5 xx xy	^α 6 ^β 6 xx yy	^α 7 ^β 7 ^γ 7 ^δ 7 xx zz yz xy	^α 8 ^β 8 ^γ 8 ^δ 8 xx yy zz xy
Τ[00 ς]	Φ1 Φ2 Φ3 Φ4	8 0 0 0 0 0 0 0	0 0 0 2 0 0 0 0	$\begin{array}{ccccc} 0 & 0 & 0 \\ 4 & 4 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{array}$	8 8 0 0 0 0 0 0 0 8 0 0 0 0 0 0	0 0 8 0 0 0 0 0	0 0 0 0 0 0 0 2	8 0 0 0 0 0 0 0 8 8 0 0 0 0 0 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
L [0 0ç]	Φ1 Φ2 Φ3 Φ4	8 0 0 0 0 0 0 0	0 0 2 0 0 0 0 0	0 0 0 8 0 0 0 0 0 0 0 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 0 8 0 0 0 0 0	0 0 0 0 0 0 2 0	0 8 0 0 0 0 0 0 16 0 0 0 0 0 0 0	0 0 0 0 0 8 0 0 0 0 0 0 8 0 0 0
Τ[ζζζ]	Φ1 Φ2 Φ3 Φ4 Φ5 Φ6 Φ7	6 2 0 0 2 -2 0 0 0 0 0 0 0 0	0 0 2 4 0 0 0 0 0 0 0 0 0 0	$\begin{array}{cccccc} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 4 & 2 & -2 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 0 6 2 0 0 0 0 0 0 2 -2 0 0	0 0 0 0 2 4 0 0 0 0 0 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
ר[נננ]	Φ1 Φ2 Φ3 Φ4 Φ5 Φ6 Φ7	$\begin{array}{cccc} 6 & -4 \\ 0 & 0 \\ 2 & 4 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ \end{array}$	0 0 2 4 0 0 0 0 0 0 0 0 0 0	$\begin{array}{cccccc} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 4 & 2 & 4 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{ccc} 0 & 0 \\ 6 & -4 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 2 & 4 \\ 0 & 0 \\ \end{array}$	0 0 0 0 2 4 0 0 0 0 0 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 2. Eight neighbor AFC composition of the interplanar force constants $\Phi_n(\xi)$ and of the elastic constants, C_{ij} , for the bcc crystal

Table 2 continued

	(111) ^α 1 ^β 1	(200) α ₂ β ₂	(220) $\alpha_{2} \beta_{2} \gamma_{2}$	(311) α _μ β _μ Υ _μ δ _μ	(222) ^{α_εβ_ε}	(400) α ₆ β ₆	(331) α ₇ β ₇ γ ₇ δ ₇	(420) ^α β ^β β ^δ β
- ×	- <u>></u>	2 7 X X	5. 5. 5 Vx zz xx	zx z/ // xx	۰ ×× ۲ ××	9 X 9 X 9 X	kx zk zz xx	x zz kk xx
	000 400	400 000	000 070 008	4 8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 4 0	040	88 0 0 0 4 0 0 0 4 0 0 0	8 0 4 0 0 8 0 0 0 4 0
	0 0 0 4 - 7 7	007	4 4 2 0 -2 0 0 0	4 8 -4 8 4 4 0 -8 0 0 0 0	0 0 7 - 4 0 0	0 7 0 0 7 0	4 4 8 0 4 4 -8 0 4 0 0 4	2 6 4 4 4 0 4 0 2 2 0 -4
	4 0 0 0 0	003	4 2 4 0 0 0 0	4 8 4 -8 4 4 0 8 0 0 0 0	040	0 7 0 0 7 0	4 4 -8 0 4 4 8 0 4 5 0 4	2 6 4 -4 4 0 4 0 2 2 0 4
	00000 00000	00000 00700	200000 20000 20000	80000 9 <u>0</u> 000 80000	00000 00000	00000 00000	90000 90000 90000	16 0 16 0 0 0 0 0
	88000 80000	0000 t	8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	8 16 8-16 0 0 0 16 0 0 -8 0 0 0 -8 0 0 0 -8 0 0 0 0 0	00000 00000	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	16 8-16 8 0 0 0 -8 0 0 16 0 0 16 0 0 0 0 0	8 16 8 0 0 0 0 0 4 0 4 0 0 0 0 0 0 -4 -4 0
	16 -4 0 0 0 0 0	0000	0 7 0 0 0 7 4 0 0 7 7 0	16 32 0 0 -4 -8 -4 8 -4 -4 0 -8 0 0 0 0	0 0 7 0 0	0 7 0 0 0 7 0 0	32 16 0 0 -4 -4 8 0 -4 -4 -8 0 -4 -4 -8 0 -4 0 0 -4	4 4 5 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7

Table 2 continued

		(11	1)	(20	0)	(220)		(31	1)		(22	2)	(40)0)		(3	31)			(42	20)		
	Φ _n (ξ)	α ₁ xx	β ₁ xy	α2 xx	^β 2 γγ	α ₃ xx	β ₃ zz	Υ ₃ xy	α ₄ xx	^β 4 γγ	Υ ₄ yz	^δ 4 ×z	^α 5 xx	^β 5 xy	α ₆ xx	^β 6 уу	α ₇ xx	^β 7 zz	^γ 7 yz	^δ 7 xy	α8 xx	^β 8 уу	γ ₈ zz	^δ 8 xy	
π ₂ [ζζ1]	Φ0 Φ1 Φ2 Φ3	16 -4 0 0	0 0 0 0	0 0 0 0	0 4 0 0	0 8 0 0	0 0 2 0	0 0 0 0	16 -4 0 0	32 -8 -8 0	0 0 0 0	0 0 0 0	0 0 4 0	0 0 0 0	0 0 0 0	0 0 4 0	32 -8 -8 0	16 0 0 -4	0 0 0 0	0 0 0 0	0 8 0 0	0 0 8 0	0 4 0 4	0 0 0 0	
π ₁ [ζζΙ]	Φ0 Φ1 Φ2 Φ3	16 -4 0 0	0 4 0 0	0 2 0 0	0 2 0 0	0 4 2 0	0 4 0 0	0 0 -2 0	16 -4 -4 0	32 -8 -4 0	0 4 0 0	0 -8 0 0	0 0 4 0	0 0 -4 0	0 0 2 0	0 0 2 0	32 -4 -4 -4	16 -4 -4 0	0 -8 8 0	0 0 4	0 2 4 2	0 6 0 2	0 4 4 0	0 4 0 -4	
C _{ij}	C ₁₁ C44 C ₁₂	2 2 -2	0 0 4	2 0 0	0 2 -2	8 4 -4	0 4 -4	0 0 8	18 2 -2-	4 20 -20	0 0 4	0 0 24	8 8 -8	0 0 16	8 0 0	0 8 -8	36 20 -20	2 18 -18	0 0 24	0 0 36	32 4 -4-	8 16 16-	0 20 -20	0 0 32	

ξ	$\omega^2 \rho = C_{\xi} q^2 (v_{\xi}^2 = C_{\xi} / \rho)$
L[001]	$\omega^2 \rho = C_{11} q^2$
τ[001]	$\omega^2 \rho = C_{44} q^2$
L[110]	$\omega^2 \rho = \frac{1}{2} (C_{11} + C_{12} + 2C_{44}) q^2$
$T_1[110]$ (polarization 11 to [110])	$\omega^2 \rho = \frac{1}{2} (C_{11} - C_{12}) q^2$
T ₂ [110] (polarization 11 to [001])	$\omega^2 \rho = C_{44} q^2$
L[111]	$\omega^2 \rho = 1/3(C_{11}+2C_{12}+4C_{44})q^2$
т[111]	$\omega^2 \rho = 1/3 (C_{11} - C_{12} + C_{44}) q^2$

Table 3. Elastic wave velocities in a cubic crystal in terms of elastic constants

expressions for $\omega_{\xi}^{2}(\vec{q})$ Equations (1.53) and (1.55) and expanding the cosine term for small ξ we get

a
$$C_{\xi} 2\pi^{2} \zeta^{2} = \sum_{n} \Phi_{n}(\xi) [1 - (1 - \frac{1}{2} (\frac{n\pi\zeta}{\zeta_{m}})^{2} + ...)]$$

a $C_{\xi} \zeta_{m}^{2} = \sum_{n} \Phi_{n}(\xi) \frac{n^{2}}{4}$. (1.57)

Thus the elastic constants can be expressed in terms of the AFC's through the interplanar force constants. For example consider the $\xi = L[00\zeta]$ mode. (This is a simple case since $C_{\xi} = C_{11}$ (from Table 3) rather than a linear combination of elastic constants as is the case for $\xi = L[110]$ for example.) From Equation (1.57)

$$a c_{11}(1) = (V4) \Phi_1(L[00\zeta]) + (1) \Phi_2(L[00\zeta]) + \dots + 9/4 \Phi_3(L[00\zeta]) + 16/4 \Phi_4(L[00\zeta])$$
(1.58)

using $\zeta_m = 1$. The AFC composition of the $\Phi_n(L[00\zeta])$'s are obtained from Table 2 and we have

a
$$C_{11} = (1/4)[8(1xx) + 16(4yy) + 8(7zz)] + (1)[2(2xx) + 8(3xx) + 8(5xx) + 8(8yy)] + (9/4[8(4xx) + 16(7xx)] + 4[2(6xx) + 8(8xx)]$$

= 2(1xx) + 2(2xx) + 8(3xx) + 18(4xx) + 4(4yy) + 8(5xx) + 8(6xx)
+ 36(7xx) + 2(7zz) + 32(8xx) + 8(8yy) (1.59)

as given in Table 2.

Force Models for the bcc Crystal

As was discussed earlier and is demonstrated in Appendix D symmetry considerations restrict the number of independent force constants. The nature of the forces between atoms may reduce the number even further by imposing additional relations between the force constants. This is the case for central forces where the forces act only between pairs of atoms and are dependent only on the separation of the pair of atoms. There exists two commonly used central force models; the axially-symmetric (AS) force model and the "central force" model (21). Both models require central forces as described above but the "central force" model is not as general as the AS model. In the context of the central force model the potential is the same for all types of neighbors in the crystal. If this potential describes the only forces existing in the crystal, the equilibrium condition for these forces imposes another condition in the force constants.

The conditions common to both the AS model and the central force model will first be discussed. From Equations (1.7c) and (1.7d)

$$\Phi_{ij}(\ell k, \ell' k') = \frac{\partial^2 \Phi(\vec{R}(\ell k))}{2 u_i(\ell k) \partial u_j(\ell' k')} \begin{vmatrix} \vec{u}(\ell k) = 0 \\ \vec{u}(\ell k) = 0 \end{vmatrix}, \quad (1.60)$$

the force constants, may be written in the form

$$\phi_{ij} = \left[\frac{\partial}{\partial u_{i}} \left(\frac{\partial \phi(R)}{\partial R} \frac{R_{j}}{R} \right) \right]_{\substack{R=R_{o}}}$$
(1.61)

where $R_j = R \partial R / \partial u_j$ = the j component of R, $R = |\vec{R}(\ell k)|$ = distance

between the two atoms of consideration (taking one atom to be at the origin) and the indices ℓ , k, etc. have been dropped. Differentiating again results in

$$\phi_{ij} = \frac{\partial^2 \Phi(R)}{\partial R^2} \frac{R_j R_i}{R_o^2} + \frac{\partial \Phi(R)}{\partial R} \frac{1}{R_o} \frac{\partial R_j}{\partial u_i} - \frac{\partial \Phi(R)}{\partial R} \frac{R_i R_j}{R_o^2}$$
$$= \phi_t \left(\delta_{ij} - \frac{R_i R_j}{R_o^2} \right) + \phi_r \frac{R_i R_j}{R_o^2}$$
(1.62)

where δ_{ij} is the Kronecker delta,

$$\phi_{t} = \frac{1}{R_{o}} \frac{\partial \Phi(R)}{\partial R} |_{R=R_{o}}$$
(1.63)

is the tangential force constant and

$$\phi_{r} = \frac{\partial^{2} \phi(R)}{\partial R^{2}} \bigg|_{R=R_{o}}$$
(1.64)

is the radial force constant. Thus for both models only two independent force constants (AFC's) exist for each type of neighbor. The mathematical constraints which reduce the AFC's to two per neighbor type are obtained from Equation (1.62). For example consider the third neighbor AFC's in the bcc crystal. For one of these neighbors, see Appendix D, Table 21, R = a/2(2,2,0) and the force constants of Equation (1.62) are given by

$$\alpha_{3} = xx = \frac{1}{2} \frac{\partial^{2} \Phi(R)}{\partial R^{2}} \begin{vmatrix} + \frac{1}{2\sqrt{2}a} & \frac{\partial \Phi(R)}{\partial R} \\ R_{o} \end{vmatrix}$$
(1.65a)

$$\beta_{3} = zz = \frac{1}{\sqrt{2}a} \frac{\partial \Phi(R)}{\partial R} \Big|_{R_{o}}$$
(1.65b)

$$\gamma_{3} = xy = \frac{1}{2} \frac{\partial^{2} \Phi(R)}{\partial R^{2}} \bigg|_{R_{o}} - \frac{1}{2\sqrt{2}a} \frac{\partial \Phi(R)}{\partial R} \bigg|_{R_{o}}$$
(1.65c)

The elimination of the partials of $\Phi(R)$ give the constraint on the third neighbor AFC's, namely,

$$xx - zz - xy = 0$$
 . (1.66)

These constraints for the AFC's to eight neighbors are given in Table 4.

The equilibrium condition of the "central force" model will now be discussed. This constraint arises from the fact that the value of the equilibrium lattice constant, a, must minimize the total potential energy of the crystal. Thus

$$\left(\begin{array}{cc} \frac{\partial}{\partial S} & \left[\sum_{n} Z_{n} \Phi(R_{n})\right] \right)_{S=a} = 0 \tag{1.67}$$

where S and R_n are the nonequilibrium values of the lattice constant and nth neighbor distance respectively (R_n = S/a $|\vec{R}(lk)|$ for lk corresponding to n) and Z_n is the number of equivalent neighbors n. From Table 21 for a bcc crystal

$$Z_i = 8, 6, 12, \dots$$
 (1.68a)

$$R_{i} = S\sqrt{3}/2, S, S\sqrt{2}, \dots$$
 (1.68b)

for $i = 1, 2, 3, \ldots$ Equation (1.67) then becomes
Neighbor	Constraint Condition	
1	none	
2	none	
3	$\alpha_3 - \beta_3 - \gamma_3 = 0$	
4	$\alpha_{i_4} - \beta_{i_4} - 8\gamma_{i_4} = 0$	
	$\gamma_4 - 3\gamma_4 = 0$	
5	none	
6	none	
7	$3\alpha_7 - 3\beta_7 + \gamma_7 - 3\delta_7 = 0$	
	$3\gamma_7 - \delta_7 = 0$	
8	$\alpha_8 - \gamma_8 - 2 \delta_8 = 0$	
	$2\beta_8 - 2\gamma_8 - \delta_8 = 0$	

Table 4.	Axially symmetric	constraints	to eighth	neighbors	for	bcc
	crystals (21)					

.

•

$$(8) (\sqrt{3}/2) \frac{\partial \Phi(R)}{\partial R} \begin{vmatrix} + & (6)(1) \frac{\partial \Phi(R)}{\partial R} \\ S=a \end{vmatrix} + (6)(1) \frac{\partial \Phi(R)}{\partial R} \begin{vmatrix} + & (12)(\sqrt{2}) \frac{\partial \Phi(R)}{\partial R} \\ S=a \end{vmatrix} = \begin{cases} R=R_{2} \\ S=a \end{cases} + \dots = 0 \qquad (1.69)$$

The derivatives of $\Phi(R)$ can be obtained by exploiting Equation (1.62) as shown in Equation (1.65b) where

$$\frac{\partial \Phi(R)}{\partial R} \begin{vmatrix} = \sqrt{2} & \alpha & \beta_3 \\ R = R_3 \\ S = a \end{vmatrix}$$
(1.70)

Table 5 gives the first and second derivatives of $\Phi(R)$ to eight neighbors. The result is the constraint for the "central force" model to eight neighbors which is

$$\alpha_{1} - \beta_{1} + \beta_{2} + 4\beta_{3} + 11\beta_{4} - 11\gamma_{4} + 4\alpha_{5} - 4\beta_{5} + 4\beta_{6} + 19\alpha_{7}$$

- 1987 + 2098 = 0 (1.71)

Using this result (Equation (1.71)) together with Tables 2 and 4 it can be verified that the constraints for the "central force" model satisfy the classic Cauchy condition for central forces in cubic crystals (21)

$$C_{12} = C_{44}$$
 (1.72)

Since the independent elastic constants for a cubic crystal are C_{11} , C_{12} and C_{44} , and if the Cauchy condition holds, only two elastic constants are required to describe the elastic properties. It can be seen from Table 2 that the elastic constants are extremely sensitive to long range forces and therefore the forces may be nearly central but fail to satisfy the Cauchy condition.

Neighbor(n)	(h ₁ h ₂ h ₃)	R _n	$\frac{\partial \Phi(R)}{2R} R=R_n$	$\frac{\partial^2 \Phi(\mathbf{R})}{2\mathbf{R}^2} _{\mathbf{R}=\mathbf{R}_{\mathbf{n}}}$
1	111	√3 a/2	√3 a (α ₁ -β ₁)/2	α ₁ .+ 2β ₁
2	200	а	aβ ₂	a ₂
3	220	√2a	√2 a β ₃	2 α ₃ - β ₃
4	311	√11 a/2	√11 a (β ₄ -γ ₄)/2	(5α4-β4)/4
5	222	√3a	√3 a(α ₅ -β ₅)	α ₅ + 2 β ₅
6	400	2a	2aβ ₆	α ₆
7	331	√19 a/2	√19 a (α7-Y7)/2	(9α7-5β7)/4
8	420	√5a	√5aγ ₈	$(4\alpha_8-\beta_8)/3$

.

Table 5. First and second derivatives of $\Phi(R)$ to eight neighbors for a bcc crystal

Lattice Dynamics and Force Model for the hcp Crystal

The analysis of the lattice dynamics of the hcp crystal proceeds in a manner analogous to that of the bcc crystal. However the situation is much more complicated since we now have two atoms per unit cell and the space group of the hcp lattice is nonsymmorphic (see Appendix C). Again, Fourier analysis techniques are applied as in Equation (1.53) which can only be applied here along Δ^1 (c or \vec{a}_3 axis). For other symmetry directions the analysis proceeds using the sum of the squares of the frequencies of the optic and acoustic branches with some modifications. As in the bcc case the force constant matrices are reduced using the symmetry operations of the particular bond in question. The force constant matrices as well as the AFC composition of the interplanar force constants are given in Appendix D.

In order to determine the AFC's we must again invoke a model. The model used here is a modification of the axially symmetric model described in the section on bcc crystals. In the axially symmetric model the AFC's are described by two forces; the bond bending and bond stretching forces of Equations (1.63) and (1.64). The modification is to take the bond stretching in the z- or c-direction different from that in the basal plane. This approach was first introduced by DeWames et al. (22) and is called the modified axially symmetric (MAS) model.

¹The reason is that Equation (1.53) applies only to crystals with one atom per unit cell. For the c-axis in the hcp crystal we can use the double zone scheme which has one atom per unit cell.

The model imposes restrictions on the AFC's, reducing the number of independent force constants in this case to 17 for 6th neighbor AFC's.

An additional constraint on the AFC's of an hcp crystal arises from the rotational sum rule or rigid body rotational invariance of Equation (1.16). This condition in the 6th neighbor MAS model is given in Appendix D. Also given in Appendix D are the elastic constraints which may be imposed on the AFC's. That is, the force constants may be forced to fit elastic constant data.

CHAPTER II. THE NEUTRON SCATTERING EXPERIMENT

In the experiments presented in this work the lattice dynamics of hcp and bcc zirconium were studied using the techniques of inelastic thermal neutron scattering. The equipment, methods and results of the measurements will be presented in this chapter. First, the furnace and cryostat used in the experiments will be described. Next, the features and calibration of the triple-axis instrument will be explained and finally in the last section the results of the measurements will be presented. Included in this last section is a description of the methods used for optimizing the instrumental parameters through the study of the differential cross section.

Furnace and Cryostat

Measurements were made on the hcp phase of zirconium at 5.5K, 295K, 773K and 1009K and on the bcc phase at 1323K and 1423K. Thus both a furnace and cryostat were required to perform the experiments.

The furnace used was specially designed for use on the triple-axis spectrometer (to be described later). That is, it was built with the criteria that it must be almost transparent to neutrons in the region of the sample and all connections (power, water coolant, vacuum lines and thermocouple leads) must be made to allow rotation of the furnace about the vertical axis through about 180° and rotation of at least a few degrees about the two horizontal axes while mounted on the sample table of the instrument.

The furnace as used consisted of an outer aluminum can 50 mils in thickness with a water jacket above and below the sample position, as seen in Figure 3. The top and bottom of the can were made of stainless steel plates which included the following features: a pumping port, thermocouple feed-throughs, electrical feed-throughs for the heating elements and several water jackets. The internal heat shielding was constructed of 10 mil niobium rolled and spot welded into concentric cylinders. These cylinders were stacked on a set of concentric niobium discs which were spaced and fastened together. Another set of discs went on top of the cylinders to complete the heat shield enclosure. Niobium was chosen for the heat shields because of its refractory characteristics - it melts at 2741K, and for its relatively small absorbtion cross section for thermal neutrons - $\sigma_A = 0.63 \times 10^{-24} \text{ cm}^2$.

The furnace was heated with two 30 mil tungsten wire filaments, wound around aluminum furnace tubes. The filaments were powered by a variable transformer with 110 VAC across the primary and an intermediate proportional controller. Feedback for the controller as well as temperature measurement was provided by two chromel-alumel thermocouples. The power required at 1400K was approximately 0.6 KW.

The vacuum system for the furnace consisted of a four inch water cooled diffusion pump and a mechanical roughing pump. A thermocouple vacuum gauge and meter were used to measure roughing vacuum and an ionization gauge and meter were used to measure the ultimate vacuum with the diffusion pump operating. Typical vacuum attained was approximately 2 x 10^{-5} torr at the temperature of the measurements.



Figure 3. Schematic diagram of furnace used in high temperature hcp Zr measurements and in bcc Zr measurements

The cryostat used for the 5.5K measurements was built for prior experiments on the triple-axis instrument. The construction of the cryostat was conventional, using liquid nitrogen and liquid helium reservoirs for cooling. Thermal shielding was provided by aluminum containers and vacuum spaces between shields and reservoirs.

During the measurements the temperature was held at $5.5K \pm 0.5K$ and was measured using a Au-Fe versus Cu thermocouple with the emf read using a potentiometer.

Triple-Axis Spectrometer

The method used to measure the phonon dispersion curves for hcp and bcc zirconium was that of inelastic thermal neutron scattering employing a triple-axis spectrometer. The following is a description of the triple-axis spectrometer, called the Triax, at the Ames Laboratory Research Reactor (ALRR), now installed at the Oak Ridge Research Reactor (ORR) at the Oak Ridge National Laboratory (ORNL). This instrument was used for all of the measurements on hcp zirconium and many of those on bcc zirconium. The remainder of the bcc measurements were performed on the triple-axis instrument HBIA which is installed at the High Flux Isotope Reactor (HFIR) at the ORNL. Comments will be made where the construction of the Triax is different from that of HBIA.

The triple-axis spectrometer performs essentially three functions in an inelastic scattering experiment: (1) neutrons of a particular energy and with a small spread in energies must be selected for the incident beam, (2) the energy of the scattered neutrons must be analyzed

to determine the energy change, and (3) the angle of scattering with respect to the incident beam and with respect to the sample must be obtained to determine the momentum change. A schematic illustration of the triple-axis spectrometer is given in Figure 4.

The neutron beam used by the instrument originates from the thermal moderator of a nuclear reactor. This beam, with a Maxwellian velocity distribution representative of a temperature on the order of 100°C, is incident on a monochromating crystal. This crystal is positioned (angles Θ_{M} and $2\Theta_{M}$) to Bragg scatter neutrons of a particular velocity or energy range ($E_{o} \pm \Delta E_{o}$).¹ This scattered beam is then collimated with cadmium Soller slits.² The momentum \vec{k}_{o} of the incident beam of energy E_{o} is determined by the direction of the beam and

$$E_{o} = \frac{\hbar^{2} k_{o}^{2}}{2m} .$$
 (2.1)

where m is the mass of the neutron.

The beam is then incident on the sample crystal set at the angle Ψ and is scattered through the angle ϕ . The scattered beam passes through another collimator and is then incident on an analyzing crystal which

¹The spread in energies is due to the finite mosaic spread of the monochromating crystal. A real crystal is not a perfect lattice throughout the entire crystal but consists of mosaic blocks with a spread in orientations about the macroscopic orientation of the entire crystal. This spread called the mosaic spread η is chosen small enough to give a reasonably small ΔE_0 but not so small as to produce a low intensity beam (for a good monochromator η is typically of the order of 0.5 degrees.

²Cadmium has an extremely large absorbtion cross section for thermal neutrons - $\sigma_A = 2650 \times 10^{-24} \text{ cm}^2$.



Figure 4. Schematic diagram of a typical triple-axis spectrometer as viewed from above

is positioned (angles Θ_A and $2\Theta_A$) for Bragg scattering neutrons of energy E_1 into the detector (to be discussed below). The final momentum of the neutron \vec{k}_0 is determined from E_1 using

$$E_{1} = \frac{\hbar^{2} k_{1}^{2}}{2m}$$
(2.2)

and the angle ϕ . Thus the neutron energy change $E_0 \sim E_1$ and momentum change $\vec{k}_0 - \vec{k}_1$ are obtained.

The detector commonly used for neutron scattering experiments, both elastic and inelastic, is a boron trifluoride (BF_3) filled proportional counter. The BF_3 counter has such advantages as a large efficiency (from 25% to 65% with 1 atmosphere of pressure) for neutrons with energies below approximately 4 Thz (1 Thz = 4.136 meV) and insensitivity to gamma-radiation. These advantages have made the BF_3 counter one of the best choices for thermal neutron detection in spectrometers and diffractometers.

The calculation and positioning of the above described angles, Θ_M , $2\Theta_M$, ψ , ϕ , Θ_A and $2\Theta_A$ for the Triax is performed by an on-line computer system consisting of a PDP 15 computer, an SDS 910 computer¹ and an interface between the computers and the control electronics of the instrument. The HBIA instrument uses a PDP 8E computer only.

¹This computer system operated three neutron spectrometers as well as experiments for other groups at the ALRR and is now operating the Triax instrument at the ORR. The purpose of the 910 between the interface and the 15 was to receive interrupts from the several different machines and make them all look the same to the 15. This function greatly simplified the program codes for the operation of the individual instruments.

Communication with the computer is via a Deckwriter. To perform a phonon measurement on the Triax the following information is entered: the number of steps on each side of the center of the scan, the number of counts at each scan point, the preset or counting interval in seconds or monitor counts (described below), a control character for selection of detector arm (the second arm has been removed from the Triax so this character is always set equal to 1), a control character to designate mode of operation; a zero for fixed E_0 or a one for fixed E_1 , fixed energy value in Thz, central \vec{Q} value, central energy value of $E_0 - E_1$, \vec{Q} increments and energy increments. A sample input for a "constant \vec{Q} " scan (to be discussed in detail in the next section) with fixed E_1 is given here:

- 5, 3, 300
- 1, 1, 3.2756
- 1, 0, -.2, .45, 0, 0, 0, .05

This scan is for a transverse [001] phonon, $\vec{Q} = (10 - .2)(q = .2)$, with eleven steps 0.05 Thz apart, centered at 0.45 Thz. The mode of operation is fixed $E_1 = 3.2756$ Thz. This is also a phonon creation experiment since $E_0 - E_1 = +0.45$ Thz. Essentially, the same information is entered on the HBIA instrument but it is restricted to fixed E_0 experiments only.

The computer calculates the angles for each step in the scan and drives each angle to its calculated position. At each step in the scan the prescribed number of counts are taken for the prescribed interval. This interval is usually determined by the rate at which neutrons are incident on the sample. This rate is measured by placing a monitor counter between the monochromating crystal and the sample. The monitor is an uranium foil detector with an efficiency of less than 0.1% which provides a method of sampling the beam without appreciable attenuation. Determining the counting interval in this manner eliminates the effect of small fluctuations in the reactor power and also of the energy dependent neutron spectrum of the reactor which affects the flux incident on the sample for fixed E_1 (and therefore varied E_0) scans. At each step in the example scan the instrument counts three times until the monitor count reaches 300 (times two prescale factors which are set manually on the instrument). These three counts are summed for each step. The output for such a scan includes the monitor preset multiplied by the prescale factors, the fixed energy E_1 , the plane of the scan (determined from the data entered into the program when the sample is mounted and aligned on the spectrometer), all angles for the initial point in the scan, and for each step in the scan the angles $\psi,\ \varphi,\ 2\Theta_{_{M}},$ each of the three individual counts, the time in seconds for each count and the sum of the three counts.

The results of a typical scan obtained using the above scheme, called a neutron group, are shown in Figure 5. To determine the center of the peak, the phonon energy, a line is first drawn through the points of the neutron group. Then a linear background is drawn under the peak. Next, the full width at half maximum (FWHM) is obtained by locating the



Figure 5. Plot of raw data for a typical neutron group

half maximum point (above background) and at this point drawing a line parallel to the background line. The length of the part of this line which is under the neutron group is the FWHM and the midpoint is the center of the peak. Occasional checks are made using a computer program which fits the neutron group to a gaussian with a linear background. The agreement between the two methods is well within the experimental error, which is determined as follows. The experimental error is essentially a measure of the left and right extremes that one could draw the line through the points of the neutron group. The error is determined as one half the difference in peak centers obtained from these two extremes.

Prior to performing an experiment on the triple-axis spectrometer the instrumental parameters must be calibrated. That is the various angles of the instrument must be determined absolutely proceeding from monochromator to sample to analyzer.

First the analyzer system is effectively removed by either setting $2\Theta_A = 0^\circ$ and either setting the analyzer crystal perpendicular to the beam, $\Theta_A = 90^\circ$, or removing the analyzer crystal entirely. In the sample position is placed a vanadium or aluminum container filled with salt in powdered form (on the order of 2-3 cm³ in volume). Aluminum and especially vanadium are used as containers in neutron scattering experiments because of their low coherent scattering amplitudes, which means they are almost transparent to thermal neutrons. Several elastic reflections from the NaCl are then measured by stepping the

angle ϕ , including at least one for $\phi = \pm \phi'$ (the same reflection on both sides of the zero setting of $\phi(=\phi_0)$). The monochromator is assumed to be set at a Θ_M , $2\Theta_M$ position such that the Bragg condition $\lambda = 2d \sin \Theta_M$ is satisfied. The exact values of Θ_M and $2\Theta_M$ and therefore λ , are not know. The two scans at ϕ' and $-\phi'$ give the exact value of ϕ_0 and thus $\phi = 2\Theta_{NaC1} + \phi_0$ for the other reflections is known. These $2\Theta_{NaC1}$ values together with the d spacings of NaC1 permit the calculation of λ from $\lambda = 2d_{NaC1} \sin \Theta_{NaC1}$. With λ the monochromator settings Θ_M and $2\Theta_M$ can be calculated. The encoders used on the instrument allow the angles to be read to within ± 0.010 . This together with an accurate knowledge of the d spacings of NaC1 and the monochromating crystal allow the determination of λ to within a few ten thousandths of an angstrom.

The next step is to mount on the sample table a single crystal of known lattice parameter and orientation. The crystal to be used in the experiment could be used here also. Two things must be accomplished in the alignment of the sample. The first is the centering of the crystal in the beam. This is checked by taking Polaroid photographs of the straight through beam at four positions of the sample angle Ψ , 90° apart. The second is the positioning of the particular reciprocal plane of the crystal of interest, parallel to the scattering plane of the instrument (horizontal). For a description of the reciprocal lattice see Appendix A. This plane is made to be horizontal by optimizing the intensities of two reflections in this plane. To permit bringing

this plane into the horizontal position the sample is typically mounted on a goniometer which has adjustments to rotate the sample about two perpendicular axes which lie in the horizontal plane. The goniometer also has horizontal translations to permit centering the sample in the beam (vertical translation is usually provided in the pedistal on which the goniometer is mounted).

Finally, using the Bragg reflections from the sample the analyzer angles can be obtained. The angles ψ , ϕ , Θ_A , and $2\Theta_A$ are first set by hand. That is, each angle is set by manually driving the angle while observing on a rate meter the variation of scattered neutron intensity with angle position. The intensity of a Bragg reflection for a typical crystal as measured on the Triax at the ALRR is of the order of 10^3 counts per second.¹ Thus the values of ψ , ϕ , Θ_A and $2\Theta_A$ are determined to within about $\pm 0.5^\circ$. At this point a computer operated scan is employed to determine the angles more precisely. The program used an iterative process sometimes called a "double-rock" to determine the Θ and 2Θ angles for a Bragg reflection. The process begins by setting one of the two angles to the manually determined Bragg peak position, 20 for example. The angle Θ is then stepped through the Bragg peak with the size of step

¹The intensity for a particular Bragg reflection depends, of course, on many factors: neutron flux incident on the crystal, incident wavelength of the neutron, the absorbtion coefficient of the crystal volume to name some of the more important ones (14).

and counting time at each step determined by the peak width and height respectively. The computer program then calculates the 0 value of the center of this peak and sets the angle to this value. A scan through the 2Θ position of the Bragg peak is then made and the angle 20 then set to the calculated center of the peak. The program repeatedly performs these 0 and 20 scans until successively determined values of both Θ and 2 Θ for the Bragg peak differ by $\Delta\Theta$ and $\Delta 2\Theta$. The values of $\Delta \Theta$ and $\Delta 2\Theta$ are input parameters in the program and are usually chosen to be about 0.02° to 0.05°, depending on the circumstances. This process, the double-rock, is performed on the sample to determine ψ and ϕ with Θ_{Λ} and $2\Theta_{\Lambda}$ set at their manually determined positions. Then $\boldsymbol{\Theta}_{\Delta}$ and $2\boldsymbol{\Theta}_{\Delta}$ are double-rocked with ψ and ϕ set at their double-rock positions. This sequence of double rocks is repeated until successive values of each angle differ by only a few hundredths of a degree.

As a final check of the calibration and sample alignment phonontype scans can be made through $\vec{Q} = \vec{\tau}$ and v = 0 (Bragg scattering). The scans used are a "constant-Q" scan, a transverse "constant-E" scan and a longitudinal "constant-E" scan all through v = 0. The "constant-Q" scan and "constant-E" scan are discussed in the next section. The above information; zeros for all angles, λ , and angles ψ and ϕ for Bragg reflections for the sample are entered into the computer program for the control of the instrument.

This calibration procedure need not be carried out for each new experiment on the instrument, but it is repeated occasionally to insure proper operating conditions for the instrument. Changes in the instrument which dictate recalibration are things such as changing the type of monochromating or analyzing crystal and changing collination of the incident or scattered beam. These changes provide flexibility to improve resolution and increase \vec{Q} (to be discussed in the last section of this chapter).

Measurements

The success or failure of a phonon measurement is critically dependent on how well the instrumental parameters are chosen to optimize the intensity of the neutron group. This optimization is achieved by careful consideration of the factors in the differential cross section for the scattering process involved and the appropriate choice of scan type and parameters which are suggested by those factors. The process involved is that of inelastic coherent neutron scattering with one phonon creation or annihilation, and expression for the differential cross section is

$$\frac{d^{2}\sigma_{1}}{d\Omega dE} = \frac{2\pi}{V} \sum_{\vec{q},\xi} \frac{k_{1}}{k_{0}} \delta(\hbar\omega + h\nu) \sum_{\vec{\tau}} \delta(\vec{Q} + \vec{q} - \vec{\tau}) \frac{\hbar(n+1/2\pm1/2)}{2\nu}$$

$$\left|\sum_{k} b_{k} \exp i(\vec{Q} \cdot \vec{X}_{k}) \times \vec{Q} \cdot \vec{U}_{k} M_{k}^{-1/2} e^{-W_{k}}\right|^{2}$$
(2.3)

51

,

where

V = volume of the unit cell, \vec{q} = phonon wave vector, $\varepsilon = phonon mode index,$ $\hbar\omega = E_0 - E_1$, the energy change of the neutron, $hv = phonon energy (v = v_{\xi}(\vec{q}), the frequency of the \xith mode at$ wave vector \vec{q}). $\vec{\tau}$ = reciprocal lattice vector (see Appendix A), $\vec{q} = \vec{k}_0 - \vec{k}_1$, the scattering vector - the momentum change of the neutron. $n = [e^{hv/kT} - 1]^{-1}$, the mean phonon occupation number, b_k = coherent neutron scattering amplitude for the k^{th} atom, \vec{X}_k = position of the kth atom of the basis with respect to the origin for the unit cell, $\vec{U}_{L} = \vec{U}(k | \vec{q}, \xi)$, displacement of the k^{th} atom for a phonon of wave vector \overrightarrow{q} and mode ξ , $M_{\mu} = mass of the k^{th} atom,$

and

 $W_k = (\vec{Q} \cdot \vec{U}_k)^2/2$, the Debye-Waller parameter for the kth atom.

The \mp and \pm signs refer to phonon creation (upper sign) and phonon annihilation (lower sign). The two delta functions require energy and momentum conservation; $\hbar\omega \mp h\nu = 0$ and $\vec{Q} \pm \vec{q} = \vec{\tau}$, respectively. There are also contributions to the scattered intensity by onephonon incoherent scattering and multiphonon scattering, the later being negligible in comparison to the one-phonon processes. These give rise to an energy dependent background which is a function of the phonon frequency distribution of the sample material.

The factors in the differential cross section which are considered in order to optimize the intensity of the neutron group will now be discussed in the context of typical scan types used for measuring the phonon dispersion curves. The most common scan type used on a tripleaxis instrument to measure v versus \vec{q} is the "constant \vec{Q} " scan. The representation of this scan in a plane of (v, \vec{q}) space is shown in Figure 6 (top). The scattering vector $\vec{Q} = \vec{k}_0 - \vec{k}_1$ is held constant while the energy change of the neutron, $\hbar \omega = E_0 - E_1$ is varied. Since

$$E_0 - E_1 = \hbar^2 / 2M(k_0^2 - k_1^2), \qquad (2.4)$$

the initial and final neutron momenta are also varied but their difference is not. Another restriction is usually imposed to simplify the situation and that is to fix either E_0 or E_1 . The Triax was usually operated in the fixed E_1 mode while the HBIA spectrometer had no means of varying E_0 and therefore always operated with fixed E_0 .

In Figure 7, the scattering geometry is shown in reciprocal space. The figure shows how \vec{k}_0 and \vec{k}_1 are varied for several steps of a "constant- \vec{Q} " scan. For each step in the scan the components of the fixed \vec{Q} are given by



Figure 6. Schematic representations of a "constant Q" scan (top) and a "constant E" scan (bottom)



Figure 7. Positions in reciprocal space of \vec{k}_0 and $-\vec{k}_1$ for several steps in a "constant Q" scan with fixed E₁. The plane shown is the (1T0) plane of the bcc reciprocal lattice

.

$$Q_{\chi} = k_{0} \cos \psi - k_{1} \cos (\phi + \psi)$$
(2.5)

$$Q_{y} = k_{0} \sin \psi - k_{1} \sin (\phi + \psi). \qquad (2.6)$$

Also, at each step in the scan the phonon energy hv is selected. Since E_1 and thus k_1 is fixed for all points in the scan, k_0 can be calculated from

$$hv = \pm \hbar^2 / 2m(k_0^2 - k_1^2) . \qquad (2.7)$$

where the +(-) sign refers to phonon creation (annihilation). Using Equations (2.5-2.7) permits the calculation of the angles ψ and ϕ for each point in the scan. (The angles Θ_M , $2\Theta_M$, Θ_A and $2\Theta_A$ are determined from E_0 and E_1 .)

Under certain circumstances it is desirable and sometimes necessary to perform constant energy transfer, $E_0 - E_1$, scans commonly called "constant E" scans (see Figure 6 bottom). In this scan, E_0 and E_1 are both fixed, thus fixing k_0 and k_1 , and \vec{Q} is varied by changing ψ and ϕ . The application of the "constant-E" method will be discussed later with respect to the bcc zirconium measurements.

With the above mode of operation of the instrument in mind, the various factors in the differential cross section are considered. The quantity

$$g_{\xi}^{2}(\vec{Q}) = \left| \sum_{k} b_{k} M_{k}^{-1/2} \exp\left(i\vec{Q}\cdot\vec{r}_{k}\right) e^{-W_{k}} \vec{Q}\cdot\vec{U}(k|\vec{q},\xi) \right|^{2}$$
(2.8)

from Equation (2.3) is called the inelastic structure factor and contains several factors important in selecting scan parameters to optimize the

intensity. The quantities b_{μ} and M_{μ} depend on the sample material only and are given for zirconium in Table 11. The dot product $\vec{Q} \cdot \vec{U}(k | \vec{q}, \epsilon)$ indicates that to optimize the intensity of the neutron group the scattering vector \vec{Q} must be parallel or nearly parallel to the atomic displacement (phonon polarization vector). For example, consider the situation illustrated in Figure 8 which shows the [1T0] reciprocal plane for a bcc lattice and the vector \vec{q} , for several phonon measurements. In each case, $\vec{\tau}$ is chosen such that $\vec{0}$ is nearly perpendicular to $\vec{U}(k|\vec{q},\xi)$. This term also suggests that the measurement be performed at the largest \vec{Q} possible; $g_{\epsilon}^{2}(\vec{Q})\alpha |\vec{Q}|^{2}$, but the competing term $e^{-W_k} = \exp -[(\vec{Q} \cdot \vec{U}_k)^2/2]$ serves to moderate such an action. The limitation in intensity at large $|\vec{Q}|$ indicated by the Debye-Waller factor was not a hindrance in these experiments since $|\vec{Q}|$ was limited by the instrumental capabilities on both the Triax and HBIA. In the case of the Triax, the low flux at the ALRR at the energies required for large $|\vec{Q}|$, negated any increase in intensity gained by increasing $|\vec{Q}|$. Physical limitations on the angles ϕ and 20_A limited $|\vec{q}|$ on HBIA. Figure 9 shows $Q^2 e^{-2W_k}$ versus Q for three temperatures for zirconium.

The inelastic structure factor also indicates that there are special reciprocal lattice points \vec{t} where the scattered intensity will be largest. This can be understood by the analogy of the inelastic structure factor with the elastic structure factor. Using the hcp lattice as an example the elastic structure factor F is maximum for



Figure 8. (1T0) plane of the bcc reciprocal lattice. The wave vectors \vec{q} for several phonons measured are shown, indicated by dashed lines. The first Brillouin zone about the origin is labeled with the standard group theoretical notation



Figure 9. Debye-Waller factor for Zr as a function of Q for three temperatures

such reciprocal lattice points as $\vec{\tau} = (002), (110)$ where $|F|^2 = 4b^2$ and less for other $\vec{\tau}$'s (see Appendix A). In fact, in the limit $v, \vec{q} = 0$ the scattering becomes elastic and $\vec{Q} \rightarrow \vec{\tau}$ which means the inelastic structure factor must go to the elastic structure factor. Thus, a rule of thumb is that the optimum $\vec{\tau}$ about which to look for accoustic phonons is also a $\vec{\tau}$ which has a large elastic structure factor.

The above reasoning for the selection of reciprocal lattice points from which to measure a particular phonon is extremely useful when calculations of the inelastic structure factor do not exist. Ideally, however, one would like to have actual calculated values of the structure factor for various $\vec{\tau}$'s and \vec{q} 's while performing the experiment. But, as can be seen from Equation (2.8), to calculate the structure factor, the eigenvectors or polarization vectors are required and to obtain these the eigenvectors or phonon frequencies are needed. Thus it is impossible to have the structure factor for the specific crystal being studied before the dispersion curves have been determined at least in part. The usual method used to circumvent this problem is to use the structure factor calculations for a crystal of like structure and if possible, similar atomic composition. Also the dispersion curves which are easiest to measure can be mapped out first using the similarities between the elastic and inelastic structure factor discussed above. When sufficient data has been collected to enable the fitting to a force constant model, the structure factor may

then be calculated for \vec{q} values of the phonon branches which are more difficult to obtain. This procedure is of course only necessary for a crystal lattice with a basis where the structure factor is nontrivial. The details of the structure factor calculation for hcp zirconium will be discussed in later sections.

The other quantities in the differential cross section that are of importance are v^{-1} , k_1/k_0 and $\hbar(n + 1/2 \pm 1/2)$. The v^{-1} factor indicates that the intensity decreases as phonon energy increases. The k_1/k_0 factor seems to show that phonon annihilation (neutron energy gain) measurements would have a larger intensity but evaluation of the population factor $n + 1/2 \pm 1/2$ indicates that phonon creation (neutron energy loss) measurements are more favorable at higher phonon energies for room temperature measurements. At 6K phonon creation measurements are the only possible choice as can be seen in Table 6.

Resolution function

The delta functions in the differential cross section imply that the neutron groups are of infinite height and zero width, but the instrumental resolution serves to lower and broaden them. The resolution of the triple-axis spectrometer has been described by several workers in as many different forms (24-28). The resolution function $R(\vec{Q},\nu)$ as defined by Cooper and Nathans (24) is the probability of detection of neutrons as a function of $\Delta\nu$ and $\Delta\vec{Q}$ when the instrument is set to measure at the point (\vec{Q},ν) in the four dimensional reciprocal space

т	ν	Popula	Population Factor ^a	
(к)	(Thz)	Creation	Annihilation	
	1.0	1.00	0.00	
6К	3.0	1.00	0.00	
	5.0	1.00	0.00	
300K	1.0	6.56	5.56	
	3.0	2.56	1.56	
	5.0	1.78	0.78	
1000K	1.0	21.00	20.00	
	3.0	7.25	6.25	
	5.0	4.57	3.57	
1400K	1.0	26.00	25.00	
	3.0	10.09	9.09	
	5.0	6.26	5.20	

Table 6. Population factor at four temperatures for phonon annihilation and creation with three different frequencies

^aPopulation factor = $\hbar(n+\frac{1}{2}\pm\frac{1}{2})$ (n = $\frac{1}{\exp(h\nu/k_BT)}$).

 (Q_x, Q_y, Q_z, v) . The usual method of visualizing this function is by considering the 50% probability ellipsoid. This is where $R(\vec{Q}, v) = 0.5Ro$ where Ro is the maximum value of $R(\vec{Q}, v)$.

As the phonon scan is made the resolution ellipsoid passes through the dispersion surface and the size and orientation of the ellipsoid with respect to the dispersion surface determines the width and shape of the neutron group. For transverse phonon measurements the scan must be performed in the "focusing" direction. That is the slope of the resolution ellipsoid as seen in the $q_t - v$ plane is nearly parallel to the dispersion curve. Figure 10 illustrates the "focused" and "defocused" scans which are the result of taking $\vec{q} = \vec{\tau} \pm \vec{q}$. Also shown is resolution ellipsoid in the $q_g - v$ plane is nearly circular and therefore no focusing effect is observed.

Another resolution effect is that of the relative scattering directions from the three crystals in the triple-axis instrument (the monochromator, sample and analyzer). The optimum condition is when the scattering is in alternating directions from each successive crystal. For example, in Figure 4, as seen by standing between the reactor and the spectrometer the scattering at the monochromator is to the right, at the sample to the left and at the analyzer to the right (RLR). The RLR configuration is obviously equivalent to the LRL configuration and any other arrangement such as RRL or RLL for example, produces a defocusing effect.



Figure 10. Resolution ellipsoid in the $\nu\text{-}q$ plane for longitudinal and transverse scans

Spurious processes

In addition to the scattering event the instrument is set to measure there are spurious processes which may contribute to the measured intensity. These processes do not merely contribute to the background as does the one phonon incoherent process for example, but they give rise to peaks in the neutron group which may shift significantly the peak due to the phonon or may be misinterpreted as phonons.

One of these processes is Bragg scattering in the monochromator and sample, and incoherent scattering in the analyzer crystal (denoted B-B-1). If this process is suspected for a particular neutron group, the measurement is repeated using a different E_0 or E_1 , or different reciprocal lattice point $\vec{\tau}$. The indications that a peak in the neutron group is the result of a spurious process are an abnormally large intensity and an unusually small FWHM. To detect these abnormalities, the widths and intensities (the area under the peak and above background) for each phonon were tabulated for comparison throughout the experiments.

Another spurious process is the B-I-B process; higher order Bragg scattering in the monochromator and analyzer, and incoherent scattering in the sample. The B-I-B conditions can be calculated in order to avoid the process entirely or to identify the process as giving rise to a peak in the neutron group. The calculation begins with the Bragg condition for the monochromator and analyzer;

$$\lambda_{Om} = 2d_{m} \sin \Theta_{M} = m\lambda_{m}$$
 monochromator (2.9)

$$\lambda_{0a} = 2d_a \sin \theta_A = a\lambda_a$$
 analyzer (2.10)

where d_m , $2\Theta_M$, d_a and $2\Theta_A$ are the plane spacing and scattering angle for the monochromator and analyzer respectively and λ_{0m} and λ_{0a} are the first order wavelengths the monochromator and analyzer are set to scatter. Besides this first order scattering, the two crystals also scatter through the same angles, $2\Theta_M$ and $2\Theta_A$, the higher order wavelengths $\lambda_m = \lambda_{0m}/m$ and $\lambda_a = \lambda_{0a}/m$ where m, $a = 2,3,4,\cdots$. Thus, for the monochromator, not only is the energy

$$E_{0} = \frac{k_{0}^{2}\hbar^{2}}{2m} = \frac{(2\pi\hbar)^{2}}{2m\lambda_{0m}^{2}}$$
(2.11)

scattered through the angle 20_{M} but also the energies

$$E_0' = \frac{(2\pi\hbar)^2}{2m\lambda_m^2} = m^2 E_0$$
 (2.12)

Similarly, the analyzer passes in addition to

$$E_{1} = \frac{k_{0}^{2}\hbar^{2}}{2m} = \frac{(2\pi\hbar)^{2}}{2m_{n}\lambda_{0a}^{2}}$$
(2.13)

the energies

$$E_{1}' = \frac{(2\pi\hbar)^{2}}{2m\lambda_{a}^{2}} = a^{2}E_{1}$$
(2.14)

when

$$E_0' = E_1'$$
 $(m^2 E_0 = a^2 E_1)$ (2.15)

for some m and a, and we get the condition for a B-1-B "phonon." The neutron energy change $\hbar\omega$ appears to be $\hbar\omega = E_0 - E_1$ and the "phonon" energy h appears to be

$$hv_{B-I-B} = \pm \hbar \omega = \pm (E_0 - E_1)$$
, (2.16)

here the + and - are for phonon creation and annihilation respectively.

Since most of the measurements in this work were phonon creation and fixed E_1 scans, eliminate E_0 in Equation (2.16) with the + sign and use Equation (2.15) to obtain

$$hv_{B-I-B} = E_1(a^2/m^2 - 1).$$
 (2.17)

Phonon creation requires that $E_0 > E_1$ which, by Equation (2.15) implies m < a. Figure 11 shows the solutions to (2.17) for several pairs of integers (m,a). To use the plot to avoid the B-1-B "contaminations" as they are sometimes called, an E_1 (horizontal axis) is selected such that around the phonon frequency of interest (vertical axis) there is no intersection with any of the lines which are solutions to (2.17). Also, a pyrolytic graphite filter (29) positioned before the analyzer was used to attenuate the higher order wavelength neutrons and thus reduce the possibility of the B-1-B process.

There is a third process which may give rise to a spurious peak in the neutron group. This process involves incoherent scattering or inelastic scattering in the monochromator which produces a contaminated beam incident on the sample. If the sample is coincidentally set


Figure 11. Several solutions for the equation for B-I-B contaminations (Equation (2.17)) for fixed E_1 and phonon creation

properly to Bragg scatter neutrons of energy E_1 , which will also be passed by the analyzer, a contaminated neutron group may be observed. This I-B-B process can be identified because the ψ and ϕ angles are those for Bragg scattering by the sample with $\lambda = 2\pi\hbar (2mE_1)^{-1/2}$. Again, repeating the measurement under different conditions usually eliminates the problem.

At the ALRR the major cause of contaminations was the B-1-B process due to the low flux of the reactor. Also pyrolytic graphite, which has a very low incoherent scattering cross section, was used for monochromating and analyzing crystals. Thus the possibility of B-B-1 or 1-B-B type contaminations are reduced using graphite.

Sample crystals

The measurements presented here on hcp zirconium were performed on a single crystal grown by 0. D. McMasters, of the Metallurgy Department of the Ames Laboratory. The crystal was prepared from high purity zirconium crystal bar purchased from Teledyne, Wah Chang. (Material in crystal bar form is poly-crystaline.) Vacuum fusion analysis showed a halfnium content of less than 100 ppm (by weight). Halfnium, which occurs naturally with zirconium, is difficult to remove from zirconium due to similar physical properties (they are both column IV transition metals). Halfnium has a large absorption cross section ($\sigma_a = 61 \times 10^{-24} \text{ cm}^2$) for thermal neutrons and therefore a high halfnium content hinders a neutron scattering experiment.

Large single crystals, 3 to 4 cm³ in volume, were grown using the following technique. The crystal bar was arc-melted into a smoothed surfaced boule. The boule was then cold rolled and scaled in an evacuated tantalum crucible. The boule was then heat treated by heating it to 1200°C in a vacuum furnace for several hours and then cooled to about 840°C. The crystal was held at this temperature for several days. The boule was then examined by standard elastic neutron diffraction techniques. Several large single crystals were located and separated with a spark cutter. The largest of these, henceforth called crystal 1, was selected for use in the hcp experiment. It was later used in the bcc experiment also.

An additional crystal (crystal 2) was purchased from Materials Research Corporation and used in the bcc experiment. This crystal was grown by the electron beam zone refining technique. Its shape was cylindrical with a 0.25" diameter and was approximately one inch in length.

After the bcc measurements on crystal 1 at the ALRR and crystal 2 at the HFIR, vacuum fusion analysis was performed on the crystals to determine hydrogen, nitrogen and oxygen content. The results of the analysis are given in Table 7. Zirconium is a gettering material and it was anticipated that oxygen contamination would present a problem. This problem will be commented on in the presentation of the bcc results later in the chapter and also in Chapter III.

Prior to experiments:		
Crystal l Hf(<u><</u>)100 ppm ^a	Crystal 2 Hf 170.0 ^a C 9.0 ^a O 11.0 H <1.00 N <1.00	
After experiments:		
Crystal 0 13000 H 35 N 610	Crystal 2 0 2900 H 22 N 4	

Table 7. Chemical analysis of crystals 1 and 2 by vacuum fusion analysis in ppm by weight

^aMass spectrographic analysis in ppm atomic.

Measurements on hcp zirconium

The measurements on the hcp phase of zirconium were performed exclusively on the Triax at the ALRR. The ALRR was a CP-5 type heavy water reactor operated at 5MW. All measurements were conducted using pyrolytic graphite crystals, set to scatter from the (002) planes, as monochromator and analyzer. Collimations used were 40' between monochromator and sample and 30' between sample and analyzer. All scans were "constant \vec{Q} " phonon creation with fixed E₁. For most scans E₁ = 3.27 Thz but larger values, up to 7.5 Thz, were used to avoid B-1-B contaminations, to reach larger \vec{Q} 's and to measure higher energy phonons. The latter was the case for the [110] optic modes near and along the zone boundary.

Phonon measurements were made at 295K, 773K and 1007K with a few selected phonons measured at 5.5K. The phonon dispersion curves were obtained in the [001], [100] and [110] symmetry directions. The measured phonon frequencies and corresponding errors are given in Table 8 and typical neutron groups are given in Figure 12. The wave vector for each phonon is given in terms of the reduced wave vector, which is defined as $|\vec{q}| = (2\pi/d_{[hkl]})\zeta$, where [hkl] is the direction of \vec{q} . Also given is $\vec{\tau}$, the reciprocal lattice point about which the given phonon was measured. The reciprocal lattice points were selected on the basis of the inelastic structure factor calculations of lyengar <u>et al</u>. (30) for magnesium. When sufficient data was collected to enable a fitting of a force constant model the structure factor was calculated for zirconium is shown in Figures 13, 14, and 15. (The corresponding reciprocal lattice planes are shown in Figures 16, 17, and 18.)

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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c} \text{TAI1[100]} & (\Sigma_{4}) \\ 0.1 & -0.1 & 0 \\ 0.2 & -0.2 & 0 \\ 0.3 & -0.3 & 0 \\ 0.4 & -0.4 & 0 \\ 0.5 & -0.5 & 0 \end{array}$		0 0 0 0	0.5 0 0 1	$\begin{array}{c c} LA[100] (\Sigma_1) \\ 0.1 & 0 & 0 \\ 0.2 & 0 & 0 \\ 0.3 & 0 & 0 \end{array}$		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	q ∓(
1100 1100 020	110	100 220 220 220	100	100	100			(ġ)
2.66±0.02			2.66±0.02				4.34±0.15	5.5K
2.56±0.03 2.98±0.02 3.59±0.04 4.28±0.05	0.83±0.01 1.53±0.01 1.97±0.06 2.21±0.03 2.33±0.06	4.17±0.06 5.02±0.06 5.31±0.06 5.36±0.05	2.56±0.03	5.14±0.04	1.68±0.03 3.23±0.03 4.18±0.03	4.75±0.07 4.85±0.08	4.61±0.04 4.60±0.05	295K
		3.52±0.20 4.84±0.18 5.03±0.15	2.32±0.15	4.78±0.10	1.53±0.05 3.01±0.06 4.04±0.10	4.71±0.10 4.68±0.10	4.87±0.08	ν±Δν 773K
		2.76±0.10 3.60±0.15 4.76±0.15 5.16±0.15	2.16±0.06	3.97±0.02 4.63±0.08	1.55±0.02 2.89±0.04 1.53±0.04	4.79±0.08 4.71±0.10 4.62±0.10 4.46±0.09	4.86±0.06	1007К

Table 8 continued

ţΦ	τ (Ġ)	5.5K	295K	v±∆v 773K	1007K
ТА <u>т</u> [110] (Т ₃)					
-0.05 -0.05 (002		0.71±0.01		
-0.1 -0.1 (0 002		1.40±0.01		1.17±0.02
-0.2 -0.2 (002		2.53±0.02		2.22 ± 0.04
-0.3 -0.3 (002		3.51±0.04		
			3.88±0.08 / E3+0 06		3.68±0.06
-0.5 -0.5 (002		4.82±0.06		4.38±0.06
10 ⁷ [110] (1 ²)					
0	003		4.62±0.08		4.86±0.08
-0.1 -0.1 (003		4.62±0.08		4.73±0.08
-0.2 -0.2 (003		4.69±0.08		
-0.3 -0.3 (003		4.20±0.06		
-0.33 -0.33 (0 003		3.92±0.08		3.68±0.06
-0.4 -0.4 (0 003		3.12±0.10		2.86±0.06
-0.5 -0.5 (003		2.67±0.06		2.38±0.06
LA[110] (T1)					
0.05 0.05 (011 0		1.50±0.02		
0.1 0.1 (011 0		2.63±0.04		
0.2 0.2 (011 0		3.70±0.06		
0.33 0.33 (0110		4.32±0.10		
0.4 0.4 (0110		4.55±0.06		
			4.62±0.06		
0.5 0.5 (011 0		4./0±0.06		
L0[110] (T4)					
000	011 0		2.58±0.08		
0.05 0.05 (0 110		3.05±0.10		
0.1 0.1 (0 020		3.90±0.05		
0.15 0.15 (0 020		4.64±0.04		
0.2 0.2 (0 020		4.94±0.06		4.75±0.08
0.3 0.3 (0.45 0.45 (0 020 020		4.64±0.08 4.95±0.12		

Table 8 continued

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0 0 0 0.1 0.1 0.15 0.15 0.2 0.2 0.3 0.3	TA11[110] (T ₄ 0.05 0.05 0.1 0.1 0.4 -0.2 0.35 0.35 -0.4 -0.4 0.45 0.45 0.45 0.45	₄₽
00000	00-00-10	+
2000		(Ĝ)
		5.5K
2.58±0.08 3.50±0.04 4.41±0.04 4.94±0.06 5.00±0.10	0.78±0.01 1.61±0.02 3.18±0.02 3.60±0.10 3.70±0.06 3.38±0.06 2.60±0.06 2.60±0.04	295K
		ν±∆ν 773K
		1007K



Figure 12. Representative neutron group for hcp Zr at 295K and 1007K







Figure 13. Inelastic scattering structure factor g_{ξ}^2 for Zr calculated using the MAS model of DeWames <u>et al.</u> (22) (Chapter III) in units of $\frac{b^2 u(\vec{q},\xi)^2 Q^2}{2m v_{\xi}}$



Figure 14. Inelastic scattering structure factor g_{ξ}^2 for Zr calculated using the MAS model of DeWames <u>et al</u>. (22) (Chapter III) in units of $\frac{b^2 u(\vec{q},\xi)^2 Q^2}{2m v_{\xi}}$





Figure 15. Inelastic scattering structure factor g_{ξ}^2 for Zr calculated using the MAS model of DeWames <u>et al.</u> (22) (Chapter III) in units of $\frac{b^2 u(\vec{q},\xi)^2 Q^2}{2m v_{\xi}}$



Figure 16. (001) plane of the hcp reciprocal lattice. The region bounded by the large hexagon is the unit over which the structure factor $g_{\xi}^2(\vec{Q})$ repeats. The first Brillouin zone about the origin is labeled with the standard group theoretical notation



Figure 17. (120) plane of the hcp reciprocal lattice. The region bounded by the dotted line is the unit over which the structure factor repeats. The first Brillouin zone about the origin is labeled with the standard group theoretical notation



Figure 18. (1T0) plane of the hcp reciprocal lattice. The region bounded by the dotted line is the unit over which the structure factor repeats. The first Brillouin zone about the origin is labeled with the standard group theoretical notation

The dispersion curves constructed from the data of Table 8 are shown in Figures 19 through 22. The solid lines through the room temperature and 1007K (Figures 19, 20 and 21) data were determined by a fitting procedure which is discussed in Chapter III. The dispersion curves had previously been measured in the [100] and [001] directions at room temperature by Bezdek <u>et al.</u> (31,32) and our room temperature data are in good agreement with those measurements. The dispersion curves in the [110] direction had not been measured prior to this work. The temperature dependence of the TA₁₁[100] branch was not measured. However, the observed temperature dependence of all other branches with one exception discussed below, was consistent with that of Moss <u>et al.</u> (33) for the TA₁₁[100].

In addition to the phonon measurements the lattice constants a and c as a function of temperature were determined from the positions of the two Bragg reflections used to align the crystal at each temperature. Figure 23 shows the values of a, c and c/a determined in the experiment along with data determined by the thermal expansion experiments of Goldak <u>et al</u>. (34).

Measurements on bcc zirconium

Measurements on the bcc phase of zirconium were begun on the Triax at the ALRR. All operating conditions were the same as in the hcp experiment. Before the dispersion curve measurements could be completed, the ALRR permanently ceased operation on December 31, 1977. When time became available on HBIA at the HFIR at the ORNL the



Figure 19. Phonon dispersion curves for hcp Zr at 295K in the symmetry directions [001], [100] and [110]. The solid lines were obtained by fitting the data to the MAS force constant model of DeWames <u>et al</u>. (22)



Figure 20. Phonon dispersion curves for hcp Zr at 295K and 1007K in the symmetry directions [001], [100] and [110]. The solid lines are an aid to the eye only



Figure 21. Phonon dispersion curves for hcp Zr at 295K and 1007K in the symmetry directions [110] and [100]. The solid lines are an aid to the eye only



Figure 22. Temperature dependence of the phonon dispersion curves of hcp Zr in the [001] direction. The solid lines are an aid to the eye only



Figure 23. Comparison of the temperature dependence of c and a determined in this work with that of Goldak <u>et al</u>. (34)

experiment was continued. Scans on HBIA were also "constant \vec{Q} " with one exception to be mentioned. As mentioned earlier, HBIA operates with fixed E₀ only. This requires phonon annihilation measurements in order to reach all but the very lowest frequency phonons since E₀ is fixed at 3.57 Thz.

The bcc single crystals were grown from the parent hcp single crystals in the vacuum furnace used for the high temperature hcp measurements. The hcp crystal was first oriented at room temperature. Then, while sitting on a Bragg reflection, the crystal was cycled through the transition temperature (approximately 1135K) several times. For crystal 1, which was used for the measurements taken on the Triax, the hcp reflection intensity was observed to decrease as the transition temperature was approached. Then, after cycling and the temperature increased above 1135K, the intensity of the bcc reflection was observed to increase. The orientation of the bcc crystal with respect to the hcp crystal for crystal 1 was found to obey the Bergers relations (35-37) for hcp to bcc transitions. In fact the process could be repeated in that the hcp single crystal was retained upon lowering the temperature through the transition. The hcp crystal could then be reoriented in order to obtain the reoriented bcc crystal.

The behavior of crystal 2 used for the measurements taken on HBIA was not so predictable. Upon cycling crystal 2 through the transition temperature, the hcp single crystal was lost. Fortunately a bcc single crystal was eventually grown and oriented but not without a great deal of difficulty.

The dispersion curve measurements on crystal 1 were made at 1323K. It was observed that the intensity of the Bragg reflections decreased with time. There are at least three possible explanations for this. The first is that the sample was simply being annealed and therefore the mosaic spread was decreasing with time. The second involves the competing ω -phase. It is possible that the amount of crystal in the ω -phase was increasing with time and therefore decreasing the amount of bcc material. The third explanation is that the oxygen impurity in the sample was affecting the Bragg intensities. This decrease in intensity prompted the measurements on crystal 2 to be made at 1423K in the event that the decreasing in the intensities was due to either the annealing or ω -phase effects. In addition, crystal 2 was sealed in a tantalum crucible under a vacuum of approximately 10^{-5} Tour in order to decrease the rate at which oxygen was absorbed by the crystal. The oxygen content of crystals 1 and 2 measured after their use in the experiments is given in Table 7. Although the oxygen impurity in crystal 2 was about 1/4 that in crystal 1, 2900 ppm (by weight) is a significant amount of oxygen (on the order of 1% atomic).

The dispersion curves at 1423K on crystal 2 were determined along the [100], [110] and [111] symmetry directions, and are shown in Figure 24. The solid line is an aid to the eye only. Table 9 gives the data from which the dispersion curves were constructed. The information is analogous to that of Table 8. Also given in Table 9 are the Triax data



Figure 24. Phonon dispersion curves for bcc Zr at 1423K in the [001], [110] and [111] directions. The solid lines are a guide to the eye only

	Crysta	al 2 da	ata (H	<mark>ВІА, 1423_</mark> К)		Cry	stal l	data	(Triax, 1323K)
	đ	τ _τ	<u>(</u> č)	v±∆v	<u></u>	p p		र्न (ढे)	ν±Δν
L[001]	<u>(Δ</u> 1)				L[001] (_{Δ1})			
0.1 0.2 0.3 0.4 0 0 0 0	0 0 0 0 0 0 0	0 0 0.5 0.6 -0.7 -1.0	200 200 200 200 002 002 002 002	$\begin{array}{c} 1.15 \pm 0.10 \\ 1.96 \pm 0.08 \\ 2.97 \pm 0.10 \\ 3.64 \pm 0.20 \\ 4.20 \pm 0.20 \\ 4.68 \pm 0.25 \\ 4.63 \pm 0.25 \\ 4.75 \pm 0.30 \end{array}$	0 0 0 0 0 0 0	0 0 0 0 0 0 0	0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8	002 002 002 002 002 002 002 002	1.06±0.03 2.05±0.05 2.91±0.03 3.58±0.04 4.21±0.04 4.56±0.15 4.62±0.20 4.66±0.20
т[001]	(∆ ₅)				T[001] (A ₅)			
0 0 0 0 0 0 0 0	0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.7 0.85	0 0 0 0 0 0 0	200 200 200 200 200 200 200 200 200	$\begin{array}{c} 0.61\pm 0.02\\ 1.20\pm 0.03\\ 1.82\pm 0.03\\ 2.58\pm 0.16\\ 2.98\pm 0.12\\ 3.40\pm 0.30\\ 4.07\pm 0.35\\ 4.18\pm 0.25\\ 4.42\pm 0.25\\ \end{array}$	0 0 0 0 0 0 0	0 0 0 0 0 0 0 0	0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.85	110 110 110 110 110 110 110 220	$\begin{array}{c} 0.56 \pm 0.03 \\ 1.18 \pm 0.03 \\ 1.81 \pm 0.05 \\ 2.36 \pm 0.06 \\ 2.97 \pm 0.10 \\ 3.70 \pm 0.12 \\ 4.15 \pm 0.15 \\ 4.39 \pm 0.30 \end{array}$
L[110]	(Σ ₁)				L[110	<u>] (Σ1)</u>			
0.1 0.2 0.3 0.35 0.4 0.45 0.5	0.1 0.2 0.3 0.35 0.4 0.45 0.5	0 0 0 0 0 0	110 110 110 110 110 110 110	1.57±0.02 3.08±0.05 4.17±0.08 4.40±0.20 4.46±0.10 4.40±0.20 4.24±0.30	0.1 -0.2 -0.3 -0.4 -0.5	0.1 -0.2 -0.3 -0.4 -0.5	0 0 0 0	110 220 220 220 220	1.67±0.04 3.14±0.10 4.30±0.15 4.36±0.20 4.28±0.40
T ₁ [110] (Σ ₄)) ^a			T ₁ [11	0] (_{Σ4})	_		
-0.1 -0.2 -0.3 -0.4 -0.5	0.1 0.2 0.3 0.4 0.5	0 0 0 0	110 110 110 110 110	0.80±0.02 1.65±0.05 2.55±0.08 3.24±0.10 3.88±0.15	-0.1 -0.2	-0.1 -0.2	0 0	1T0 1T0	0.76±0.04 1.58±0.08

Table 9. Phonon frequencies for bcc Zr (1 Thz = 4.136 meV)

^aPolarization 11 to [1T0].

Table 9 continued

Crysta	1 2 dat	a (HE	BIA, 1423K)		Crys	tal 1	data (1	Triax, 1323K)
q	<u>τ</u> (<u>č)</u>	v±∆v				र (ढे)	ν±Δν
T ₂ [110] (Σ ₃)) ^b			T ₂ [11	0] (Σ ₃))		
-0.1 -0.1 -0.2 -0.2 -0.3 -0.3 -0.4 -0.4	0 0 0	002 002 002 002	0.86±0.04 1.72±0.04 2.49±0.06 3.14±0.10	-0.1 -0.2 -0.3 -0.4	-0.1 -0.2 -0.3 -0.4	0 0 0	002 002 002 002	0.77±0.02 1.65±0.03 2.43±0.06 3.18±0.10
0.5 0.5 T[111] (Λ ₃)	U	002	4.20±0.25	0.5 T[111	ο.5] (Λ ₃)	U	002	J.4J±0.20
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0.1 0.2 0.3 -0.4 -0.5 0.6 -0.7 0.8 -0.9	002 002 002 222 003 002 112 002	$\begin{array}{c} 0.70 \pm 0.02 \\ 1.45 \pm 0.05 \\ 2.10 \pm 0.20 \\ 2.70 \pm 0.15 \\ 3.40 \pm 0.30 \\ 4.00 \pm 0.20 \\ 4.23 \pm 0.20 \\ 4.52 \pm 0.25 \\ 4.75 \pm 0.20 \end{array}$	-0.1 -0.2 -0.3 0.4 -0.5 -0.6	-0.1 -0.2 -0.3 0.4 -0.5 -0.6	0.1 0.2 0.3 -0.4 0.5 0.6	112 112 112 112 112 002	0.64±0.04 1.31±0.10 1.94±0.20 2.60±0.30 3.30±0.30 3.44±0.40
$L[111](\Lambda_1)$				L[111] (A ₁)			
-0.1 -0.1 0.2 0.2 -0.3 -0.3 -0.4 -0.4	-0.1 0.2 -0.3 -0.4	111 110 112 112	2.22±0.05 3.94±0.20 4.63±0.20 4.31±0.20	-0.1 -0.2 -0.3 -0.4	-0.1 -0.2 -0.3 -0.4	-0.1 -0.2 -0.3 -0.4	111 111 111 111	2.09±0.04 3.96±0.30 4.44±0.40 4.32±0.20
Constant AE scans				(Constar	nt∆E s	cans	
ζ	Ť (Ğ)	ΔE	·	ζ		(G)	Δ Ε
$\begin{array}{c} 0.562 \pm 0.02 \\ 0.588 \pm 0.015 \\ 0.614 \pm 0.012 \\ 0.672 \pm 0.015 \\ 0.658 \pm 0.015 \\ 0.676 \pm 0.010 \\ 0.706 \pm 0.015 \\ 0.738 \pm 0.02 \\ 0.794 \pm 0.025 \end{array}$	22 22 22 22 22 22 22 22 22 22 22 22 22	22 22 22 22 22 22 22 22 22 22 22 22 22	2.80 2.30 1.80 1.20 0.70 1.80 2.30 2.80 3.50	0.541 0.589 0.632 0.650 0.700 0.715 0.762 0.826	±0.01 ±0.01 ±0.01 ±0.01 ±0.01 ±0.01 ±0.01 ±0.01		222 222 222 222 222 222 222 222 222 22	2.80 2.30 1.80 1.20 1.80 2.30 2.80 3.50

^bPolarization 11 to [001].

Table 9 continued

Crystal 2	data (H	BIA, 1423K)	Crystal	data	(Triax, 1323K)
q	र्ने (दे)	ν±Δν	q	र्ने (दे)	ν±Δυ
-0.9 -0.9 -0.9 -1.0 -1.0 -1.0	222 222	4.50±0.35 4.75±0.30	-0.9 -0.9 -0.9	222	4.24±0.40

from crystal 1 at 1323K. Figure 25 shows typical neutron groups for crystals 1 and 2. The agreement is quite remarkable since the two sets of data were taken using different crystals and scan modes on different spectrometers. (From the results of the hcp measurements, one would not expect a large difference in results for the 1323K and 1423K data.)



Figure 25. Representative neutron groups for bcc Zr at 1323K (Triax) and 1423K (HBIA)

CHAPTER III. ANALYSIS AND DISCUSSION

Data Analysis for the hcp and bcc Experiments

Although a great deal of information about a crystal can be obtained directly from the measured dispersion curves, there is additional information which may be extracted from this data. Specific thermodynamic properties such as the lattice specific heat and Debye temperature can be calculated once the dispersion curves have been measured. The procedure begins with the fitting of the data, usually to a Born-von Kármán force model as discussed in Chapter I, to obtain a set of calculated AFC's. The AFC's have very little physical significance in the analysis since they are a phenomenological representation of the largely unknown interatomic forces. This is especially true for metallic crystals where the contribution of the itinerant electrons complicates the picture even further. Once the AFC's have been calculated, $\omega_{F}(\vec{q})$ may be evaluated for any mode ξ and any \vec{q} . Thus the AFC's are in a sense only part of an interpolation scheme to obtain a continuous $\omega_{F}(\vec{q})$ as a function of \vec{q} . Then the phonon density of states is calculated from the continuous dispersion curves. The density of states is then used in the calculation of the lattice specific heat.

We begin with the analysis of the bcc data since the techniques used are much less involved. The analysis of the hcp data is covered next followed by a discussion of the anomalies in the dispersion curves of hcp and bcc Zr.

bcc fitting procedure

The computer program used to analyze the bcc data was a linear least squares fitting routine acquired from McMasters University, Ontario, Canada. The program was the same as the fcc program used by Gould (38) but with the appropriate modifications for a bcc crystal. The detailed operation of the program is given in Reference 38 and only an outline of its description is givn here.

The program uses a given set of data, the phonon frequencies, $\omega_{\xi}(\vec{q})$, and corresponding errors to obtain a set of AFC's which minimize the quantity

$$\sigma^{2} = \sum_{\xi \vec{q}} W(\xi, \vec{q}) [m \ \omega_{\xi}(\vec{q})^{2} - \sum_{p} \phi_{p}(\xi, \vec{q}) f_{p}(\xi, \vec{q})]^{2}$$
(3.1)

(see Equation (1.53)). The $W(\xi, \vec{q})$ is a weighting factor which takes into account the error of a particular phonon frequency and is of the form

$$W(\xi,\vec{q}) = \left[\frac{1}{\omega(\xi,\vec{q})(\Delta\omega(\xi,\vec{q}))}\right]^2 \qquad (3.2)$$

The ϕ_p 's are the AFC's and $f_p(\xi, \vec{q})$, the fitting function, is given by

$$f_{p}(\xi, \vec{q}) = \sum_{n} \alpha_{np} \left(1 - \cos \frac{n\pi\zeta}{\zeta_{m}} \right) , \qquad (3.3)$$

where the α_{np} 's are the coefficients of the AFC decomposition of the Φ_n 's given in each row of Table 2.

The program allows the AFC's to be fit to elastic constant data as well. This is accomplished by adding a term in Equation (3.1) as

follows

$$\sigma'^{2} = \sigma^{2} + \sum_{j} W^{c}(j) [a c_{j} c_{m}^{2} - \sum_{p} \phi_{p} f_{p}^{c}(j)]^{2}$$
(3.4)

where $W^{C}(j)$ is the weighting factor for the particular C_{j} . The quantity $f_{p}^{C}(j)$ is the elastic constant fitting function obtained from Equation (3.4) as

$$f_p^{c}(j) = \sum_{n \neq 0} \alpha_{np} n^2 / 4$$
 (3.5)

Minimizing σ'^2 with respect to the AFC's results in a set of AFC's consistent with the data and/or the given elastic constants. The elastic constants for bcc zirconium have not as yet been measured and therefore the above program option was not utilized.

Also provided in the program is the capability of fitting the data with the additional axially symmetric (AS) constraints of Table 4 and with any given set of AFC's fixed at some value. The terms added to Equation (3.4) for the AS constraints and AFC fixing constraints are

$$\sum_{m} W''_{m} \left(\sum_{n} \beta_{nm} \phi_{n}\right)^{2} , \qquad (3.6)$$

 β_{nm} defined in Table 4 and

$$\sum_{m} W'_{m} \left(h_{m} - \sum_{n} \delta_{n} \phi_{n} \right)^{2} , \qquad \delta_{n} = 1 \text{ for } n = m \qquad (3.7)$$
$$= 0 \text{ for } n \neq m$$

respectively. The W' and W'' are inputed weighting factors for the two types of constraints. Thus if all the constraints of Table 4 are

imposed a fit results which is consistent with the axially symmetric model.

The relative importance of the data or a particular constraint in the fit is determined partly by the weighting factors $W(\xi, \vec{q})$, $W^{C}(j)$, W'_{m} and W''_{m} (Equations (3.1), (3.4), (3.6), and (3.7)) and by the number of data points and constraints.

In this fitting scheme the AFC's are obtained essentially from the AFC composition of the interplanar force constants. Therefore only as many AFC's may be obtained as there are IFC's. From Table 2 it can be seen that for the three major symmetry direction $[00\zeta]$, $[\zeta\zeta 0]$, and [[[c[ccccf line since there exist degeneracies at the high symmetry points Γ , H, and P. At I all seven branches are degenerate and there are only three independent elastic constants. Therefore there must be four relations (7 - 3 = 4) between the IFC's. At H there are four degenerate branches with one frequency. Thus there are three more relations (4 - 1 = 3)between the IFC's. Similarly another relation is introduced at P where two branches are degenerate (2 - 1 = 1). There is one additional relation due to setting all $\phi_n = 0$ for n > 8. There are therefore only 22 independent IFC's (31 - 4 - 3 - 1 - 1 = 22) but from Table 2 there are 23 independent AFC's for 8 neighbors. Thus, to obtain an eight neighbor fit additional constraints must be imposed. The alternative is to measure a few frequencies in the $\left[\frac{1}{2}\frac{1}{2}\zeta\right]$ or $\left[\zeta\zeta\right]$ directions. Also the fitting for n \leq 7 may be made with no additional constraints and is called a general tensor fit.

Once the set of AFC's have been calculated from the fitting routine the program calculates a frequency for each of the inputed measured phonons using Equation (1.53). The "goodness" of the fit is then indicated by the value of χ^2 evaluated from

$$\chi^{2} = \frac{1}{N} \sum_{i=1}^{n} \left(\frac{\omega_{\xi}(\vec{q})_{calc} - \omega_{\xi}(\vec{q})_{exp}}{\Delta \omega_{\xi}(\vec{q})_{exp}} \right)^{2}$$
(3.8)

where the sum is over all data points and N is the number of data points minus the number of fitting parameters.

Several of the fitting techniques used to analyze the data are listed below.

- 1) 1 to 7 neighbor; general tensor
- 1 to 7 neighbor; modified tensor (one AS constraint each of the 7 AS constraints used)
- 3) 1 to 8 neighbor; modified tensor (three AS constraints)
- 4) 1 to 8 neighbor; axially symmetry (all 7 AS constraints)
- 5) 1 to 7 neighbor; (one and two AFC's fixed at values from general tensor fit)

The χ^2 value for the general tensor fit is shown in Figure 26 as a function of neighbor. The 7 neighbor general tensor fit had one of the lowest χ^2 values of all the fits and the AFC's from this fit were used in the continuation of the data analysis. The dispersion curves obtained from this fit are plotted in Figure 27 along with the experimental data. The agreement between the experimental and calculated frequencies is excellent in the [00 ζ] direction and in the [$\zeta\zeta$ 0] direction except near



Figure 26. Variation of X^2 with the number of neighbors included in the 7 neighbor general tensor fitting procedure


Figure 27. Phonon dispersion curves for bcc Zr calculated from the 7 neighbor general tensor fitting procedure

the zone boundary for the longitudinal branch, an anomaly to be discussed later. The region of poorest agreement is the [$\zeta\zeta\zeta$] direction for ζ from 0.5 to 1.0. This problem is obviously the result of trying to fit the anomalous dip at $\zeta \cong 2/3$.

The AFC's, IFC's and elastic constants obtained from the 7 neighbor general tensor fit are tabulated in Table 10.

bcc phonon density of states

The method used to calculate the phonon frequency distribution function $g(\omega)$ or phonon density states (DOS) is that of Gilat and Raubenheimer (39). The DOS program first uses the AFC's from the fitting program to give the dynamical matrix at a set of \vec{q} values that form a cubic mesh in an irreducible section of the Brillouin zone (see Appendix A Figure 42). The dynamical matrix is then used to solve for the eigenfrequencies at the cubic mesh points. The constant energy surfaces inside each cube are then approximated by parallel planes which means $g(\omega) d\omega$ is proportional to the volume between the two planes at ω and $\omega + d\omega$. Therefore by selecting an appropriate number of mesh points and a small enough d ω the program can very accurately obtain $g(\omega)$.

Some of the features of the dispersion curves may cause dramatic features to be present in the DOS. This can be seen by examining the form of $g(\omega)$ (40)

$$g(\omega) d\omega \sim \int \frac{dS_{\omega}}{\nabla \to \omega} d\omega$$
 (3.9)

AFC	10 ⁴ dynes/cm	(error)	IFC ^a	τ[001]	L[001]		
lxx	0.79583	0.04038					
lxy	0.47259	0.04540	Φ_1	6.70882	6.93466		
2xx	0.73283	0.07862	Φ2	-0.66202	1.90336		
2yy	-0.23570	0.05291	Фз	0.09284	-0.13300		
3xx	0.15018	0.02861	Φ_4	-0.04328	-0.29958		
3zz	-0.00690	0.04063		- 57	- []	7	
3xy	0.24337	0.04447		$T_1[110]$	$T_2[110]$		
4xx	0.04630	0.04222	Φ_1	3.88716	3.59894	6.30096	
4yy	0.02793	0.02509	Ф ₂	-0.57598	-0.51044	0.92767	
4yz	-0.33868	0.02043	Φз	-0.00968	0.06052	-0.24201	
4xz	0.03233	0.02035		т[111]	L[111]		
5xx	-0.09547	0.02053	Φ_1	6.42387	1.51674		
5xy	0.23409	0.04148	Ф ₂	0.41822	-0.98634		
6xx	0.03452	0.07432	Фз	-0.29958	6.60014		
буу	-0.02164	0.03447	$\Phi_{l_{4}}$	0.08266	1.54288		
7xx	-0.03146	0.01031	Φ5	0.24989	-0.17352		
7zz	0.01513	0.01184	Φ_{6}	0.42748	-1.14170		
7yz	-0.11624	0.01495					
7×y	-0.02904	0.01283					
Elastic Constants		10	2 dynes	/cm ²			
	C ₁₁ C ₄₄ C ₁₂		0.99970 0.29072 0.45379				
(C_{11})	$-C_{12}-C_{44})/3$	(0.27888				
(C ₁₁	-C ₁₂)/2		0.27296				
(c ₁₁	+C ₁₂ +2C ₄₄)/2		1.01746				

Table 10. AFC's, interplanar force constants (IFC's) and elastic constants obtained from seven neighbor general tensor fit

^a (FC's in units of 10^4 dynes/cm.

where dS_{ω} is an element of area on the constant frequency surface ω . From the factor $\nabla_{q}\omega$ in the denominator $g(\omega)$ is expected to become very large as $\nabla_{q}\omega \rightarrow 0$ or in other words as the constant energy surface becomes parallel to \vec{q} . If we consider \vec{q} in one of the symmetry directions then $\nabla_{q}\omega$ is simply the slope of the dispersion curve and we expect $g(\omega)$ to become large as the slope of the dispersion curve goes to zero. Although the behavior of $g(\omega)$ is determined by phonons in off symmetry directions as well as in the symmetry directions, flat regions along the dispersion curves usually produce some structure in the DOS.

The density of states for bcc Zr calculated using the AFC's of the 7 neighbor general tensor fit is shown in Figure 28. The spike at 4.5 Thz apparently corresponds to the L[$\zeta\zeta$ 0] branch near the zone boundary (Figure 24). The broad peak at 4.4 Thz may be due to the local minima and maxima in the L[$\zeta\zeta\zeta$] branch around $\zeta = 0.8$ but the width of the peak makes positive identification difficult.

bcc thermodynamic analysis

The method used here to calculate the lattice specific heat of bcc Zr is much simpler than that used for hcp Zr since the phonon dispersion curves we measured at a single temperature only. To obtain the relation for the specific heat we begin with the expression for the lattice vibrational energy of a crystal (40,41)

$$U = \int g(\omega) n(\omega) \hbar \omega d\omega \qquad (3.10)$$

where $n(\omega)$ is the phonon occupation number of Equation (2.3) and the integration is over the nonzero frequency range of $g(\omega)$. The lattice



Figure 28. Phonon density of states of bcc Zr at 1423K determined from the AFC's generated by the 7 neighbor fit

specific heat at constant volume (per mole), C_V^{ℓ} , is related to the density of states by

$$\frac{C_{V}^{\ell}(T)}{3N_{O}k_{B}} = \left(\frac{\partial U}{\partial T}\right)_{V} = \int \frac{(\beta\hbar\omega)^{2}g(\omega)\exp(\beta\hbar\omega)d\omega}{\left[\exp(\beta\hbar\omega) - 1\right]^{2}}$$
(3.11)

where $\beta = 1/k_B^T$ and N_O is Avogadro's number. The integral in Equation (3.11) may be evaluated numerically at any temperature given the phonon density of states $g(\omega)$. Using the DOS described in the previous section, $C_V^{L}(T)$ for bcc Zr was calculated and is shown in Figure 29. Notice that although bcc Zr does not exist below 1135K, $C_V^{L}(T)$ was evaluated down to OK.

Direct calorimetric measurements of the specific heat at constant pressure C of bcc Zr have been made (8,42). This makes comparison of the calculated C_V with direct measurements possible through the relation

$$c_{p} = c_{V} + c_{d}$$
$$= c_{V}^{\ell} + c_{V}^{e} + c_{d}$$
(3.12)

where C_V^e is the electronic contribution to the specific heat at constant volume. The dilation term C_d is obtained from the thermodynamic relation

$$c_{V} = \frac{K}{(9\alpha^{2}VT + KC_{p})} c_{p}^{2}$$
, (3.13)

or



Figure 29. Temperature dependence of the lattice specific heat of bcc Zr

$$C_{d} = C_{p} - C_{V} = 9\alpha^{2} VT/K$$
 for $C_{p}/C_{V} \cong 1$ (3.14)

where α is the coefficient of linear thermal expansion, V is the specific volume (atomic volume) and K is the adiabatic compressibility. The compressibility is the inverse of the bulk modulus and for a cubic crystal is given in terms of elastic constants by

$$B = 1/K = 1/3(C_{11} + 2C_{12}) \qquad (3.15)$$

Since neither an experimental value of the compressibility nor experimental values of the elastic constants were available the appropriate slopes of the dispersion curves were used to calculate C_{11} and C_{12} (see Tables 3 and 10). The resulting value for the bulk modulus of bcc Zr at 1423K calculated from Equation (3.15) and the values of C_{11} and C_{12} from Table 10 was B = 0.664 x 10¹² dynes/cm². With the values of α as a function of temperature (43) $C_d(T)$ was calculated from Equation (3.14). The electronic contribution to the specific heat at constant volume was obtained by using the electronic DOS of bcc Zr of Myron <u>et al</u>. (44) and is shown in Figure 30 (top).

In Figure 30b we show the calculated specific heat at constant pressure, $C_p(calc) = C_V^{\&} + C_V^{e} + C_d$, plotted along with the direct measurement $C_p(meas)$ of Hultgren <u>et al</u>. (8) and Vollmer <u>et al</u>. (42). Considering the disagreement between the two measured C_p 's, the calculated specific heat for bcc Zr is quite acceptable.



Figure 30. Temperature dependence of the electronic specific heat of bcc Zr (top figure). Comparison of the specific heat at constant pressure with that of various workers (8,42)

hcp fitting procedure

The MAS model of DeWames <u>et al</u>. (22) was used in the analysis of the hcp data. The phonon frequencies are nonlinear functions of the force constants in this model. This means that there is not a unique set of force constants which minimize χ^2 (Equation (3.8)). Thus by using a nonlinear fitting routine with different initial starting parameters one may obtain a different set of force constants. For this reason a program was developed by Harmon and Arch (45) which sampled the parameter space for parameters within a given range at random points at which the χ^2 test was performed. Typically on the order of 30,000 points were tested and the set of parameters with the lowest χ^2 was used in the nonlinear fitting program.

The success of the fitting procedure was judged on the agreement between the measured phonon frequencies and elastic constants and those calculated using the force constants obtained from the fit. For this reason fits were made using the 295K and 1007K data both with and without the elastic constants fixed. As can be seen from the plot of the calculated and measured frequencies in Figures 19, 20 and 21, the calculated and measured (12) elastic constants in Table 11, the fits at 295K and 1007K are quite acceptable. Also given in Table 11 are the MAS force constants (see Appendix D) for the four fits described. For all fits the condition deduced from rotational invariance (Equation (1.16) and (D.28)) was satisfied.

	(10) ⁴ dynes/cm)		- <u> </u>					
MAS force constants	295K no elastic constraints	295K elastic constraints	1007K no elastic constraints	1007K elastic constraints					
K(1,12)	3.974	3.979	5.341	7.276					
C _{Bx} (1,12)	-0.377	-0.354	-0.648	-1.467					
$C_{Bz}^{(1,12)}$	-1.288	-1.292	-2.132	-3.395					
к(2,11)	2.280	2.266	2.762	3.620					
C _{Bx} (2,11)	-0.070	-0.048	0.093	0.904					
$C_{B_{Z}}^{(2,11)}$	0.328	0.324	0.062	0.038					
K(3,12)	-0.460	-0.500	0.448	0.295					
C _{Bx} (3,12)	-0.039	-0.030	-0.122	0.600					
$C_{Bz}^{(3,12)}$ K(4,11)+	-0.145	-0.126	-0.368	-0.301					
$C_{p_{-}}(4,11)$	0.840	0.650	0.520	0.310					
$C_{P,1}^{BZ}(4,11)$	0.043	0.039	0.034	0.030					
K(5,12)	0.195	0.152	-0.592	-0.1056					
C _{RV} (5,12)	0.028	0.036	0.197	0.288					
C _{B7} (5,12)	-0.026	-0.013	0.149	0.258					
к(6,11)	0.148	0.127	0.418	0.688					
C _{Bx} (6,11)	0.171	0.167	-0.323	-0.1021					
C _{Bz} (6,11)	0.010	0.002	0.008	-0.010					
(10 ¹² dynes/cm ²)									
Elastic constants	295K ^a no elastic constraints	295 elastic constraints	1007 ^a no elastic constraints	1007 elastic constraints					
$C_{11} = C_{12} = C_{13} = C_{44} = C_{33} = C$	1.508 0.833 0.840 0.324 1.857	1.434 0.728 0.653 0.320 1.648	1.207 0.702 0.795 0.232 1.614	1.114 0.832 0.656 0.228 1.414					

Table 11. MAS force constants (see Appendix D) for four fits

^aFrom Ref. (12).

hcp phonon density of states

The method used to calculate the hcp phonon DOS was again that of Raubenheimer and Gilat (46) with the extension to hcp crystals. The force constants of the first column of Table 11 were used in this calculation with the resulting phonon DOS of Figure 31.

Two identifications appear possible in the DOS of hcp Zr. The first large peak in the DOS at about 2.5 Thz is probably due to the flat regions in the TO[001] and possibly also the TA₁ and TA₁[100] branches near M. Also the flat region of the LO[001] and TO₁[100] near Γ probably give rise to the peak at about 4.7 Thz.

The phonon density of states will be used later in the thermodynamical calculations.

hcp thermodynamic analysis

As mentioned in the introduction the specific heat of zirconium exhibits anomalous behavior above room temperature. For this reason it is interesting to use the results of the phonon measurements to calculate the lattice specific heat. Thus, it can be determined if the temperature dependence of the phonon dispersion curves is consistent with the direct measurement of the specific heat.

The entropy at temperature T of an anharmonic crystal can be calculated using

$$S^{(\ell)} = -k_{B} \sum_{\sigma}^{3n} \{\beta \hbar \omega_{\sigma}(T)n_{\sigma} + \ln(n_{\sigma} + 1)\}$$
(3.16)

where k_{R} is Boltsman's constant, σ stands for (\vec{q},j) the wave vector and



Figure 31. Phonon density of states of hcp Zr at 295K

branch index of the phonon mode, $\hbar\omega_{\sigma}(T)$ is the quasiparticle (phonon) energy, $\beta = 1/kT$ and

$$n_{\sigma} = \left[\exp(\beta \hbar \omega_{\sigma}(T)) - 1 \right]^{-1} . \qquad (3.17)$$

This is the usual harmonic formula with the harmonic frequencies replaced by the "renormalized effective frequencies" $\omega_{\sigma}(T)$ (47,48). Within the framework of low-order perturbation theory the $\omega_{\sigma}(T)$ agree with the frequencies determined by inelastic neutron scattering and this expression for the entropy can be used to calculate the lattice specific heat at constant pressure (47,48). From Equation (3.16)

$$C_{p}^{(\ell)} = \frac{\partial S^{(\ell)}}{\partial T} \bigg|_{\substack{\text{constant} \\ \text{pressure}}} = Nk_{B} \sum_{\sigma}^{3n} \frac{\chi_{\sigma}^{2}}{\sinh^{2}\chi_{\sigma}} \bigg[1 - \bigg(\frac{\partial \ln \nu}{\partial \ln T}\bigg) \bigg]$$
(3.18)

where $\chi_{\sigma} = h\nu/2k_{\rm B}T$. The first term is the quasiharmonic contribution $C_{\rm p}^{(\ell)}(\rm QH)$ and approaches the classical value of $3\rm Nk_B$ in the hightemperature limit. The second term is the anharmonic contribution. Anharmonicity manifests itself in the explicit temperature dependence of the phonon frequencies. Also, from Equation (3.18) it can be seen that in order to calculate $C_{\rm p}^{(\ell)}$ as a function of T, the phonon frequencies and their temperature derivatives are needed. Since only a relatively small number of phonon frequencies were measured and at only a few temperatures suitable interpolation schemes are necessary to use Equation (3.18) to evaluate $C_{\rm p}^{(\ell)}$. The fitting procedure of the previous section yields a continuous set of phonon frequencies at a given temperature in the appropriate symmetry directions of the Brillouin zone. The interpolation method used to calculate the thermodynamics of Cu and Pd by Miiller and Brockhouse (49) was applied to obtain the temperature derivatives of the frequencies. In this method, the temperature dependence of the frequencies is expressed in the form

$$v_{\sigma}(T) = v_{\sigma}(T_{j})f(T)$$
(3.19)

where T_1 is an arbitrary reference temperature, taken here to be 295K. The average temperature dependence f(T) is defined experimentally as

$$f(T) \equiv \left\langle \frac{\nu_{\sigma}(T)}{\nu_{\sigma}(T_{l})} \right\rangle = \frac{1}{n} \sum_{\sigma}^{n} \frac{\nu_{\sigma}(T)}{\nu_{\sigma}(T_{l})}$$
(3.20)

where n is the number of modes measured at the temperature T_{l} and T. As can be seen from Figure 32 the experimental frequencies vary linearly with temperature, which means that f(T) is merely the average slope of v_{σ} (T) versus T. Using Equations (3.18), (3.19) and (3.20), the specific heat can be written

$$c_{p}^{(l)} = 3Nk \left[1 - T \frac{f'(T)}{f(T)} \right] \int g(v, T_{1}) \frac{\chi^{2}}{\sinh^{2}(\chi f(T))} dv \qquad (3.21)$$

where $g(v,T_1)$ is the phonon frequence distribution (density of states), Figure 31, which was discussed in the previous section. The lattice specific heat calculated using Equation (3.21) is shown in Figure 33 along with the quasiharmonic contribution $C_p^{(l)}(QH)$. It can be seen that there is a large contribution to $C_p^{(l)}$ from the explicit temperature dependence of the phonon frequencies. Before this



Figure 32. Temperature dependence of the frequencies of some phonons of hcp Zr



Figure 33. Temperature dependence of the lattice specific heat at constant pressure evaluated using the Miiller-Brockhouse interpolation scheme (47). $C_p^{(\ell)}(QH)$ is the quasiharmonic lattice specific heat given by the first term of Equation (3.18)

calculation can be compared to direct measurements of C_p , the electronic specific heat $C_p^{(e)}$ must be added. First, though, the use of an average temperature dependence is evaluated.

In view of the anomalous temperature dependence of the zone center upper optic mode, the interpolation method of Equations (3.19) and (3.20) must be justified since Cu and Pd show no such anomaly. Justification was provided by several calculations, the first of which uses the high temperature limit ($\chi_{\alpha} \ll 1$) of Equation (3.18)

$$c_{p}^{(\ell)} \cong 3Nk_{B} \left[1 - \left(\frac{\partial \langle \ln v \rangle}{\partial \ln T} \right)_{p} \right]$$
 (3.22)

where $\langle \ln v \rangle = \int g(v,T) \ln v dv$. The lattice specific heat was evaluated at 773K and 1007K using Equation (3.22). The average value of $\ln v$, $\langle \ln v \rangle$ was evaluated using the frequency distributions at 295K, 773K and 1007K. The slope of $\langle \ln v \rangle$ vs. $\ln T$ (notice the linearity in Figure 34) was used in Equation (3.22). The values of $C_p^{(\ell)}$ at 773K and 1007K calculated in this manner agreed to better than 2% with those of the previous calculation using the average temperature dependence of the frequencies f(T).

An additional check was made by calculating the heat capacity using the quasiharmonic approximation (3.16) where the temperature dependence of the frequencies is expressed as

$$v_{\sigma}(T) = v_{\sigma}^{(h)} + \Delta_{\sigma}(T) , \qquad (3.23)$$

the $\Delta_{\sigma}^{}(T)$ being the shifts from the harmonic frequencies. The anharmonic



Figure 34. Temperature dependence of <1n ω > evaluated using Equation (3.22b)

contribution to the entropy, correct to lowest order in perturbation theory, is given by

$$\Delta S = -\hbar \sum_{\sigma} \left(\frac{\partial n_{\sigma}}{\partial T} \right) \Delta_{\sigma}(T)$$
 (3.24)

where $n_{\sigma} = (\exp h\nu/k_{B}T - 1)^{-1}$ is evaluated at the harmonic frequencies $\nu_{\sigma} = \nu_{\sigma}^{(h)}$. The contribution to $C_{p}^{(l)}$ is then

$$c_{p}^{(\ell)} = \hbar T \sum_{\sigma} \frac{\partial^{2} n_{\sigma}}{\partial T^{2}} \Delta_{\sigma}(T) + \frac{\partial n_{\sigma}}{\partial T} \frac{\partial \Delta_{\sigma}(T)}{\partial T} . \qquad (3.25)$$

As mentioned previously, the phonon frequencies varied linearly with temperature. Therefore $\Delta_{\alpha}(T)$ is of the form

$$\Delta_{\sigma}(T) = \alpha_{\sigma}T$$
 (3.26)

where α_{σ} is the slope of $\nu_{\sigma}(T)$ versus T and the harmonic frequencies $\nu_{\sigma}^{(h)}$ can be obtained by extrapolation to OK. The anharmonic contribution to $C_{p}^{(l)}$ calculated using Equation (3.25) was added to $C_{p}^{(l)}(QH)$ calculated with the frequency distribution determined by the harmonic frequencies $\nu_{\sigma}^{(h)}$. The specific heat evaluated using this approach was found to agree to better than 2% with that obtained using the interpolation method of Miiller and Brockhouse (49).

A much better test of the interpolation method of Equation (3.20) is the direct calculation of the entropy since both Equation (3.18) and Equation (3.25) involve approximations. The entropy was calculated directly from Equation (3.16) using the measured frequency spectra at 295K, 773K and 1007K. A comparison of the entropy calculated in this way to the entropy calculated using the interpolation method of Miiller and Brockhouse shows agreement to within 1% at 773K and 4% at 1007K.

Finally, the electronic specific heat $C_p^{(e)}$ was calculated and added to $C_p^{(l)}$ in order for comparison to direct measurements of C_p . A band theoretical calculation (44) was performed to obtain the electronic density of states (Figure 35) from which the electronic specific heat was calculated (shown in Figure 36). Notice the large increase of $C_V^{(l)}$ above $\gamma(0)$ T, the linear extrapolation from low temperatures. This increase is due to the increase of the effective electronic density of states at the Fermi level with increasing temperature. The sum $C_p^{(e)} + C_p^{(l)}$ is shown in Figure 37 along with the direct measurements of C_p by various workers (8,9,10,11). The agreement is quite good in view of the fact that there are discrepancies, on the order of 10% in some instances, among the values of C_p measured by the various workers.

Discussion of hcp Dispersion Curves

The temperature dependences of the frequencies of all branches, Figures 20, 21 and 22, except the zone center upper optic mode to be discussed later, are as expected; decreasing frequency as the temperature, and therefore volume, increase. However the changes in the frequencies are much larger than can be accounted for by the thermal expansion effect. In fact, estimates of the frequency shifts using the thermodynamic Grüneisen parameter (34) are only 0.1 to 0.2 times the observed shifts. Such strong temperature dependence implies that the phonon frequencies have mostly an explicit temperature dependence.





Figure 36. Temperature dependence of the electronic specific heat of hcp Zr



Figure 37. Comparison of the specific heat at constant pressure $C_p = C_p^{(e)} + C_p^{(l)}$ (dashed line) with experimental results of various workers (8-11). The dash-dot line is the specific heat obtained by using the electronic contribution of Shimizu and Katsuki (50)

The frequency shifts given in Table 8, for a particular branch, are generally larger for lower q. Also, the elastic constants at room temperature and 1007K given in Table 11, calculated from the slopes of the low q linear region of the acoustic branches, agree very well with the measured values of the elastic constants (12). Since the elastic constants depend strongly on long range forces, it appears that the large frequency shifts for low q phonons are due to changes in long range forces determined by the electronic response to the nuclear motion. This implies that the temperature dependence of the phonon frequencies is intimately related to the structure of the electronic density of states near the Fermi level. The electronic states near the Fermi level are the most important in screening of nuclear motion and are affected most by changes in temperature.

As the temperature was increased towards the hcp \rightarrow bcc transition temperature (1135K) there were no systematic significant changes in the widths of the neutron groups. Also, there was no precipitous decrease observed in any of the p¹⁻ on frequencies. These two observations suggest that the hcp \rightarrow bcc transition from below is first order, a conclusion consistent with that of Moss et al. (33).

The most striking aspect of the dispersion curves, the exception mentioned above, is the zone center upper optic mode behavior.¹ From the dispersion curves in the [001] direction (Figure 22) it can be seen

From now on this mode will be referred to as LO[001] although the TO[100] and TO[110] exhibit the same behavior for $\hat{q} \rightarrow 0$.

that frequencies of the LO[001] branch at and near the zone center decrease with decreasing temperature. This is called soft mode behavior and is sometimes a precursor to a structural phase transition. For this reason measurements of this branch were also taken at 5.5K to determine just how dramatic this dip at the zone center might become. A similar but much more pronounced dip is exhibited at room temperature in the same branch of technetium (51) which has the highest superconducting transition temperature ($T_c \sim 8K$) of the hcp elements.

Ideally the results of the hcp experiment should be described in using the microscopic theory of lattice dynamics (52,53). Using the microscopic framework the results could be related to the electronic band structure of the metal. However at its present stage of development the microscopic theory has not been used for any realistic calculations at finite temperatures. In order to make more quantitative the argument presented earlier for the connection between the temperature dependent frequencies and the electronic band structure, Harmon and Stassis (54) have performed a frozen phonon calculation. The electronic band structure of hcp Zr was calculated using the LAPW method (55,56) with the nuclei displaced in the manner of the zone center L0[001] mode. The nuclei were placed in sites along the c-axis 5% closer than in the normal lattice. The following discussion, still more qualitative than quantitative, is based on the frozen phonon calculations.

The electronic density of states (DOS) of Zr has a large peak just above the Fermi level (Figure 35) originating from bands of predominantly d character. As the temperature is increased the DOS at the Fermi level,

the effective DOS, increases due to this peak. This is evident from the calculated electronic heat capacity which rises above the linear constant DOS electronic heat capacity $\gamma(0)T$ (see Figure 36). The increase of the effective DOS with increasing temperature adds to the usual electron screening in metals of the ionic charges. This effect decreases the long range forces and lowers the phonon frequencies with increasing temperatures. Such behavior is consistent with the implications of the temperature dependence of the phonon frequencies and elastic constants discussed earlier.

The anomalous behavior of the zone center LO[001] mode arises from a situation unique to the hcp lattice. The electronic bands for wave vectors in the AHL plane (reciprocal lattice basal plane) are doubly degenerate. There is some spin orbit splitting but it is very small. Performing the band calculation with the frozen phonon displacements which reduce the crystal symmetry shows that the degeneracies are split. This is true for any phonon displacements in general but the splittings are largest with those of the L0[001] phonon. The results of the calculation show that the band near H at the Fermi level is split such that the upper band rises above the Fermi level and is therefore unoccupied and the lower band falls below the Fermi level and remains occupied. The net effect on the total energy of the crystal would be zero if both bands were equally occupied but since the upper band is totally unoccupied (at T = 0) the crystal energy is lowered. Thus the energy associated with the LO[001] phonon is lowered (on the order of a few meV). The splitting is on the order of 1000K so that as the

temperature is increased the occupation of the upper band increases, wiping out the reduction in the crystal energy from the split bands.

Discussion of bcc Dispersion Curves

The dispersion curves for bcc Zr show instances of anomalous behavior, some of which are not observed in other bcc transition metals. One anomaly is the degenerate, to within experimental error, $T_1[\zeta\zeta 0]$ and $T_2[\zeta\zeta 0]$ branches. This behavior implies that the elastic shear moduli C_{44} and $\frac{1}{2}(C_{11} - C_{12})$ are equal (see Table 3) or in other words bcc Zr exhibits isotropy for the propagation of elastic waves. This observation is consistent with the conditions favoring the mechanism for the bcc to hcp transition (see Appendix B). Tungsten (57) is the only other bcc transition metal which exhibits this behavior and since Ti and Hf also undergo hcp to bcc transitions it is expected that their bcc phases are isotropic also.

Another anomaly is the dip in the L[$\zeta \zeta 0$] branch as \dot{q} approaches the zone boundary point N. This behavior may be related to the zone center upper optic mode anomaly at hcp Zr since the (001) hcp plane transforms to a (110) bcc plane.

The most dramatic feature of the dispersion curves is however the pronounced valley in the L[$\zeta\zeta\zeta$] branch at $\zeta = 2/3$. Due to the finite resolution of the triple axis instrument the minimum frequency of this valley was impossible to determine. Constant energy transfer neutron groups taken in attempt to find the bottom of the dip are shown in Figures 38 and 39 for crystals 1 and 2 on the Triax and HBIA instruments



Figure 38. "Constant E" (neutron energy loss) scans through $\vec{q} = 2/3$ [111] obtained with crystal 1 on the Triax



Figure 39. "Constant E" (neutron energy gain) scans through $\dot{\vec{q}} = 2/3[111]$ obtained with crystal 2 on HBIA

respectively. No other bcc element ever examined has shown such behavior although sodium (58), tantalum (59), niobium (60), and iron (61) do show less dramatic but similar behavior of the L[$\zeta \zeta \zeta$] branch.

Fortunately there exists other experimental data which is very revealing as to the behavior of the L[2/3 2/3 2/3] mode. Examining the dispersion curves of niobium (60), molybdenum (62) and Nb-Mo alloys (in an extensive study of the lattice dynamics of these alloys by Powell <u>et al</u>. (63)) shows that the entire phonon spectrum and especially the L[2/3 2/3 2/3] mode soften dramatically in going from Mo to bcc Zr (see Figure 40). This softening correlates with the decrease in the number of electrons outside closed shells from 6 for Mo to 4 for bcc Zr. Thus it is probable that the behavior of the L[2/3 2/3 2/3] mode for bcc Zr is a manifestation of the electronic structure of the crystal.

As mentioned in the introduction there is a competing bcc to ω phase transition in pure Zr under pressure and in Nb-Zr alloys. In principle this transition occurs through the softening of a single phonon, namely the L[2/3 2/3 2/3] (64,65). Therefore the observed behavior of this mode for bcc Zr supports the suggestions that the bcc to ω -phase transition is electronically driven and proceeds presumably through charge density waves.



Figure 40. L[111] branches of Mo (62), Nb (60) and bcc Zr

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APPENDIX A. RECIPROCAL LATTICE AND ELASTIC STRUCTURE FACTOR FOR THE bcc AND hcp CRYSTALS

Reciprocal Lattice to the bcc Lattice

The direct lattice primitive basis vectors of the bcc lattice are shown in Figure 41 and are expressed as:

$$\vec{a}_1 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$
, (A.1a)

$$\dot{a}_{2} = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z})$$
, (A.1b)

$$\dot{\vec{a}}_{3} = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z})$$
, (A.1c)

where \hat{x} , \hat{y} and \hat{z} are unit vectors in the x, y and z directions respectively, and a is the lattice constant in angstroms. The formulae for the reciprocal lattice basis vectors are (40):

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$
, (A.2a)

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$
, (A.2b)

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$
 (A.2c)

From Equations (A.La)-(A.2c) we obtain:

$$\vec{b}_1 = \frac{2\pi}{a} (\hat{x} + \hat{y})$$
 (A.3a)

 $\vec{b}_2 = \frac{2\pi}{a} (\hat{y} + \hat{z})$ (A.3b)

$$\vec{b}_3 = \frac{2\pi}{a} (\hat{x} + \hat{z})$$
 (A.3c)



Figure 41. Direct lattice primitive basis vectors of the bcc lattice

which are the primitive lattice vectors of the fcc lattice.

Thus the fcc lattice is the reciprocal lattice of the bcc lattice. Also, note that $\vec{a}_i \cdot \vec{b}_j = \delta_{ij} 2\pi$ for i, j = 1,2,3. (A.4) The general reciprocal lattice vector denoted \vec{G} or $\vec{\tau}$ is then

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$
 (A.5a)

$$= \frac{2\pi}{a} [(h+\ell)\hat{x} + (h+k)\hat{y} + (k+\ell)\hat{z}].$$
 (A.5b)

From Equation (A.4) we note that $\vec{G}_{hkl} \cdot \vec{\chi}_{mnp} = 2\pi (integer)$ where $\vec{\chi}_{mnp} = m\vec{a}_1 + n\vec{a}_2 + p\vec{a}_3$. (A.6)

The first Brillouin zone is formed by the set of planes which are perpendicular to the twelve shortest nonzero \vec{G} 's,

$$\frac{2\pi}{a} (\pm \hat{x} \pm \hat{y}) , \frac{2\pi}{a} (\pm \hat{y} \pm \hat{z}) , \frac{2\pi}{a} (\pm \hat{x} \pm \hat{z}) , \qquad (A.7)$$

and located at their midpoints. The zone is a regular twelve-faced solid, a rhombic dodecahedron, as shown in Figure 42. Also indicated in this Figure are the points and lines of high symmetry (see Appendix C). The irreducible volume of the zone is defined by the points Γ , H, N and P.

There is some confusion with the reciprocal lattice of the bcc and fcc lattices for the following reason. When the Miller indices hkl are used for an fcc or bcc crystal they are not the hkl of Equation (A.4) but are those referred to the simple cubic lattice. For example the [001] direction in a bcc crystal is not in the \vec{b}_3 direction ($\hat{x}+\hat{y}$) but is in the \hat{z} direction. With respect to this convention the reciprocal lattice vectors are

$$\vec{G} = \frac{2\pi}{a} \left[h\hat{x} + k\hat{y} + l\hat{z}\right] . \tag{A.8}$$



Figure 42. First Brillouin zone of the bcc reciprocal lattice. The points and lines of high symmetry are labeled with the standard group theoretical notation

Using this convention, the various planes of atoms are very simple to see; the planes x=0, y=0, z=0 are (001) type planes, the planes x= \pm y, y= \pm z, z= \pm x are (110) type planes, etc. Figures 8 and 43 show the (1T0) and the (001) planes¹ in reciprocal space. Again the points and lines of high symmetry are indicated.

Elastic Structure Factor of the bcc Lattice

The elastic structure factor squared appears in the expression for the total coherent scattering per unit cell of a crystal (14). The elastic structure factor of the unit cell for the hkl reflection, \vec{G}_{hkl} , is given by (37)

$$F(hk\ell) = \sum_{i} \overline{b}_{i} \exp(-i \vec{\chi}_{i} \cdot \vec{G}_{hk\ell})$$
(A.9)

where \vec{b}_i = coherent neutron scattering amplitude for the ith atom, $\vec{\chi}_i$ = position of ith atom of the basis with respect to the origin of the unit cell. Since we are now using the simple cubic unit cell and not the primitive unit cell for the bcc lattice, the crystal has a basis with atoms at 000 and $\frac{1}{2}$ (components along ax, ay and az). Thus, Equation (A.6) becomes

$$F(hk\ell) = \overline{b} \{1 + \exp[-i\pi(h+k+\ell)]\}$$
(A.10)

which has the following values

$$F(hkl) = 0$$
 when $h+k+l = odd$ integer (A.11a)

$$F(hkl) = 2f$$
 when $h+k+l - even integer$ (A.11b)

¹A plane in reciprocal space is either denoted by the direction perpendicular to it, such as: the perpendicular to the (1TO) and (001) planes are the [1TO] and [001] directions respectively; or by the two directions lying in the plane, such as: the (1TO) and (001) planes are also called the [110]-[001] and [100]-[010] planes respectively.

The forbidden reflections (Equation A.8b) are a manifestation of the use of the simple cubic cell instead of the primitive unit cell for the bcc lattice. Therefore, points such as (001), (111) and (210) are not reciprocal lattice points, \vec{G} 's, and instead lie on the zone boundary of some Brillouin zone (see Figures 8 and 43).

Reciprocal Lattice to the Hexagonal Lattice

The direct lattice primitive basis vectors are shown in Figure 44 and can be written

$$\vec{a}_1 = \sqrt{3}/2a\hat{x} + \frac{1}{2}a\hat{y}$$
, (A.12a)

$$\dot{\vec{a}}_{2} = -\sqrt{3}/2a\hat{x} + \frac{1}{2}a\hat{y}$$
, (A.12b)

$$\vec{a}_3 = c\hat{z}$$
 (A.12c)

where a and c are the hexagonal lattice constants. The atomic positions are given by Equations (1.5b) and (1.5c) where

$$\vec{x}(k) = 0$$
 for k=1 ,
 $\vec{x}(k) = 2/3\vec{a}_1 + 1/3\vec{a}_2 + 1/2\vec{a}_3$ for k=2

Applying the reciprocal lattice formulae (Equations A.2a, b and c), the reciprocal lattice basis vectors we obtain

$$\vec{b}_1 = \frac{2\pi}{a} \left(\frac{1}{\sqrt{3}} \hat{x} + \hat{y} \right)$$
 (A.13a)

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$$\vec{b}_2 = \frac{2\pi}{a} \left(\frac{-1}{\sqrt{3}} \hat{x} + \hat{y} \right)$$
 (A.13b)

$$\vec{b}_3 = \frac{2\pi}{c} \hat{z}$$
 (A.13c)

which also form a hexagonal lattice and are shown in Figure 45 along with points and lines of high symmetry. The irreducible volume of the cell is



Figure 43. (001) plane of the bcc reciprocal lattice. The wave vector \vec{q} for the measurement of the T₁[110] branch is shown. The first Brillouin zone about the origin is labeled with the standard group theoretical notation





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Figure 45. First Brillouin zone of the hcp reciprocal lattice. The points and lines of high symmetry are labeled with the standard group theoretical notation

defined by the points Γ , M, K, A, L and H. Again the general reciprocal lattice vector \vec{G} or $\vec{\tau}$ is

$$\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$
 (A.14)

As was the case for the bcc lattice we have for the hexagonal lattice $\vec{b}_i \cdot \vec{b}_j = \delta_{1j} 2\pi$ for i, j = 1,2,3 (Equation A.15) and $\vec{G}_{hkl} \cdot \vec{\chi}_{mnp} = 2\pi$ (integer) (Equation A.16) where $\vec{\chi}_{mnp} = m\vec{b}_1 + n\vec{b}_2 + p\vec{b}_3$.

Elastic Structure Factor of the hcp Crystal

The hcp lattice is the hexagonal lattice with a basis of two identical atoms located at 000 and $\frac{2}{3} \frac{1}{3} \frac{1}{2}$ (components along the \vec{a}_i). Equation (A.10) becomes

$$F(hkl) = \overline{b}\{1 + \exp[-i(2/3\vec{a}_1 + 1/3\vec{a}_2 + \frac{1}{2}\vec{a}_3) \cdot (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)]\} (A.17)$$

Using Equation (A.15), F(hkl) becomes

$$F(hkl) = \overline{b} \{1 + \exp[-2\pi i(\frac{2h+k}{3} + \frac{l}{2})]\}$$
(A.18)

Then

$$\begin{split} |F(hkl)|^2 &= 0 \quad \text{for } 2h+k = 3(\text{integer}), \ l \ \text{odd}; \ (hkl)=(001), \dots, \ (A.19) \\ &= \overline{b}^2 \quad \text{for } 2h+k = 3(\text{integer})\pm 1, \ l \ \text{even}; \ (hkl)=(100), \dots, \\ &= 3\overline{b}^2 \quad \text{for } 2h+k = 3(\text{integer})\pm 1, \ l \ \text{odd}; \ (hkl)=(101), \dots, \\ &= 4\overline{b}^2 \quad \text{for } 2h+k = 3(\text{integer}), \ l \ \text{even}; \ (hkl)=(002), (110) \dots. \end{split}$$

Since we have a basis, we again have forbidden reflections as in the bcc case.

Plane Spacings for Hexagonal and Cubic Lattices

The plane spacings $d_{hk\ell}^{}$ for hexagonal lattices are given by

•

$$d_{hkl} = \left[\frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}\right]^{-\frac{1}{2}}$$
(A.20)

and for cubic lattices by

$$d_{hkl} = \left[\frac{h^2 + k^2 + l^2}{a^2}\right]^{-\frac{1}{2}}$$

APPENDIX B. bcc TO hcp TRANSITION

During the growing procedure used in obtaining the bcc phase of zirconium (in Crystal 1), the relations between the planes of the hcp phase and those of the bcc phase were established. These relations were found to agree with those of Burgers (35) and are as follows:

bcc hcp

$$(110) \leftrightarrow (002)$$

 $(110) \leftrightarrow (100)$ (B.1)
 $(002) \leftrightarrow (110)$

That is, in the bcc to hcp transition a (110) bcc plane becomes a (002) hcp plane, another (110) type bcc plane, perpendicular to the first, becomes a (100) type hcp plane and a (002) type bcc plane, perpendicular to both of the (110) type bcc planes becomes a (110) type hcp plane which is perpendicular to the (100) hcp plane. A specific example is the following:

	bcc	hcp	
(110) type	∫(ITO)	(002)	
bcc planes	Υ (110)	(100)	(B.2)
•	° (002)	(T20) } (110) type hcp plane	

According to Burgers the bcc to hcp transition takes place in the following manner, as depicted in Figure 46. Figure 46a shows five bcc unit cells positioned such that a (110) plane is horizontal. Marked by heavy lines, is a prism which becomes the hcp unit cell after the transition. The sides of the prism are formed by {112} bcc planes and the ends by {110} bcc planes. The primary shear of the transition is along a {112} bcc plane in the corresponding [111] direction (e.g. the [111] direction is parallel to the (112) plane). This shear, shown in Figure



Figure 46. bcc to hcp transition. (a) bcc lattice, (b) primary shear of the bcc to hcp transition, (c) hcp lattice

.1

46b, changes the acute angle in the basal parallelogram of the prism from 70.53° to 60° .

There remain other smaller atomic motions to complete the transition the primary one being that of the atom in the center of the prism. This atom must move in the [100] or [T00] direction to a position directly above the center of gravity of one of the equilateral triangles formed by the atoms in the base of the prism as shown in Figure 46c. Also, the dimensions of the sides of the prism must be altered by contraction or dilation to become those of α -Zr at the transition temperature. For example, the sides of the basal parallelogram are unequal because of the shear process; the sides parallel to the shear direction [111] are unaltered while the other sides have increased in length (by a factor of sin 109.47°/sin 120°=1.09).

The stiffness modulus for the above described (112) [111] shear in a cubic crystal is given by (12)

$$C_{(1|2)[1|1]} = 1/3(C_{11} - C_{12} + C_{44})$$
 (B.3)

This modulus is minimum with respect to the two principal shear moduli C_{44} and $\frac{1}{2}(C_{11} - C_{12})$ when

$$2C_{44}/(C_{11} - C_{12}) = 1$$
 (B.4)

That is, the (112)[111] shear if favored in an isotropic bcc crystal.

APPENDIX C. GROUP THEORY IN LATTICE DYNAMICS

Group Theoretical Techniques

Application of the techniques of group theory in order to exploit the symmetry properties of the crystal lattice, greatly simplifies lattice dynamical calculations. In this section these techniques will first be explained and then applied to the bcc and hcp crystal structures. The method (and notation) adopted here will be that of Venkataraman <u>et al</u>. (17) who use the multiplier-representation approach (66,67).

The eigenvalue equation we wish to solve is Equation (1.20)

$$D(\vec{q})\vec{u}(\vec{q},\xi) = \omega_{\xi}^{2}(\vec{q})\vec{u}(\vec{q},\xi)$$
(C.1)

The solution is obtained for each individual \vec{q} of interest in the Brilloun zone. When working with only a particular \vec{q} (in lattice dynamics or band structure) it is valid to consider $G(\vec{q})$, "the group of the wave vector" (68). This group, which is a subgroup of the space group of G of the crystal, is formed by the elements of $G, R_{(m)} = [\underline{R}]\vec{x}(m) + \overline{v}(R)]$ for which the following relation holds

$$R\vec{q} = \vec{q}$$
 or $\vec{q} + \vec{G}$ (C.2)

where \vec{G} is a reciprocal lattice vector. Therefore, the elements of $G(\vec{q})$ are those of G whose rotational part <u>R</u> acting on \vec{q} leave it invariant. Also an element of $G(\vec{q})$ acting on the crystal leaves the direction of a wave traveling along \vec{q} unchanged or change it by \vec{G} . The elements of $G(\vec{q})$ still posses their translational part and thus $\Im = \{[E|x(m)]\}$ the translational group, is a subgroup of $G(\vec{q})$. In adopting the "multiplierrepresentation" (MR) approach, the situation is further simplified by the use of the point group of \vec{q} , G (\vec{q}) and its "irreducible multiplier representations" (IMR). The elements of $G_{0}(\vec{q})$ are simply the rotational parts of the elements of $G(\vec{q})$, $G_{0}(\vec{q}) = \{R\}$.

Before discussing the multiplier representation as applied to lattice dynamics, the description of a MR in general is appropriate. The set of matrices $\{\underline{\tau}(R_i)\}$ form a "multiplier representation" of the group G under the following conditions:

(1) for each element $R_{i} \in G$ there is associated a matrix $\underline{\tau}(R_{i})$

(2) $\underline{\tau}(R_i)\underline{\tau}(R_j) = \Phi(R_i,R_j)\underline{\tau}(R_iR_j)$ for all $R_i,R_j\epsilon G$. The $\{\Phi(R_i,R_j)\}$ from the corresponding factor system for the MR. If the matrices $\underline{\tau}(R_i)$ are irreducible the MR $\{\underline{\tau}\{R_i\}\}$ is called an "irreducible multiplier representation" (IMR).

The outline of the procedure to be used is as follows:

- 1. The set of matrices which commute with $\underline{D}(\vec{q})$ will be constructed. They form a reducible MR RMR of $G_{D}(\vec{q})$.
- 2. The RMR of $G_{q}(\vec{q})$ is decomposed in terms of the IMR's of $G_{q}(\vec{q})$.
- 3. The "symmetry-adapted" vectors are constructed. These transform just as the eigenvectors of $\underline{D}(\vec{q})$.
- 4. The dynamical matrix is block diagonalized through the similarity transformation indicated by the symmetry adapted vectors.

This is the ultimate goal of the application of group theory to the eigenvalue problem of Equation (C.1).

Construction of matrices

The matrices which commute with $\underline{D}(\vec{q})$ are constructed by considering the transformation properties of the eigenvectors of $\underline{D}(\vec{q})$, $\vec{e}(\vec{q}|j)$. The detailed method of obtaining the form of these matrices is given in (17) and only the results are presented here. The components of the $3n\times3n$ matrix, $\underline{T}(\vec{q},\underline{R})$, associated with the element \underline{R} of $G_{O}(\vec{q})$ are

$$T_{\alpha\beta}(kk'|\vec{q};\underline{R}) = R_{\alpha\beta}\delta(k,F(k',R)) \exp\{i\vec{q}\cdot[\vec{x}(k)-\underline{R}\vec{x}(k')]\}$$
(C.3)

 α,β = 1,2,3 and k,k¹ = 1,...n

where the $R_{\alpha\beta}$ are the components of <u>R</u> and the Kronecker delta $\delta(k, F(k', R))$ depicts the interchange of sublattices. F(k', R) is the sublattice reached from k' via $R_m = [\underline{R} | \vec{x}(m) + \vec{v}(R)]$. The $\underline{T}(q, \underline{R})$ have the following properties:

- 1. $\underline{T}(\vec{q},\underline{R})$ is unitary; $\underline{T}(\vec{q},\underline{R})^+ = \underline{T}(\vec{q},\underline{R})^{-1}$
- 2. $\underline{T}(\vec{q},\underline{R})$ commutes with $\underline{D}(\vec{q})$; $\underline{T}(\vec{q},\underline{R})\underline{D}(\vec{q})\underline{T}(\vec{q},\underline{R})^{\dagger} = \underline{D}(\vec{q})$ for all $\underline{R} \in G_{n}(\vec{q})$
- 3. $T(\vec{q}) = \{\underline{T}(\vec{q},\underline{R})\}$ forms a 3n dimensional RMR of $G_{0}(\vec{q})$ with the corresponding factor system $\Phi(\vec{q}) = \{\Phi(\vec{q}_{j};\underline{R}_{i},\underline{R}_{j})\}$ where $\Phi(\vec{q}_{j};R_{i},R_{j}) = \exp\{iG(\vec{q},R_{i})\cdot\vec{v}(R_{j})\}$.

It is appropriate at this time to point out the simplifications in the scheme brought about by special values of \vec{q} and particular lattices. For example, consider a crystal symmetry with a symorphic space group and one atom per primitive unit cell, (n=1) such as a bcc crystal. Then the $T_{\alpha\beta}(kk' | \vec{q}; \underline{R})$ becomes

$$T_{\alpha\beta}(\vec{q};\underline{R}) = R_{\alpha\beta}$$
 (C.4)

since k takes only one value and $\vec{x}(k)$ can be taken to be zero with an

appropriate choice of axis. Also, $\Phi(\vec{q}; \underline{R}_i, \underline{R}_j) = 1$ since $\vec{v}(\underline{R}_j) = 0$ for all \underline{R}_j (for a symmorphic space group). This means that the IMR are identical to the IR in this case. Antoher simplification occurs even for nonsymmorphic groups when \vec{q} is within the BZ and thus $\vec{G}(\vec{q}, R_i) = 0$. Again the multipliers $\Phi(\vec{q}; \underline{R}_i, R_i) = 1$ and the IMR reduce to the ordinary IR.

Decomposition of $T(\vec{q})$

The decomposition of $T(\vec{q})$ is of the form

$$T(\dot{q}) = \sum_{s} c_{s} \tau^{s}(\dot{q})$$
(C.5)

where the $\tau^{s}(\vec{q})$ are the IMR of $G_{o}(\vec{q})$, C_{s} is the number of occurrences of $\tau^{s}(\vec{q})$ and the sum is over all IMR's of $G_{o}(\vec{q})$. C_{s} is determined through the use of the expression

$$C_{s} = \frac{1}{h} \sum_{\substack{X \in G_{o}(\vec{q})}} [x^{s}(\vec{q} \underline{R})] * x(\vec{q} \underline{R}) , \qquad (C.6)$$

where h is the order of $G_{\alpha}(\vec{q})$ and

$$\chi(q;\underline{R}) = \operatorname{Tr}\underline{T}(\overrightarrow{q};\underline{R}) , \quad \chi^{S}(\overrightarrow{q};\underline{R}) = \operatorname{Tr}\underline{T}^{S}(\overrightarrow{q};\underline{R}) . \quad (C.7)$$

The relation
$$3n = \sum_{s} c_{s} f_{s}$$
, (C.8)

where f_s is the dimensionality of $\tau^{s}(\dot{q})$, is useful as a check when all C_{s} 's have been evaluated.

The implication of Equations (C.5) and (C.6) is that there are C_s eigenvalues $\omega_{s,1}^2(\vec{q}), \omega_{s,2}^2(\vec{q}), \ldots, \omega_{s,c_s}^2(\vec{q})$, each being f_s -fold degenerate. The eigenvectors for this set of eigenvalues are denoted

$$\omega_{s1}^{2}(\vec{q}) \neq \{\vec{e}(\vec{q};s,1,1), \vec{e}(\vec{q};s,1,w), \dots, \vec{e}(\vec{q};s,1,f_{s})\}$$

$$\omega_{s2}^{2}(\vec{q}) \neq \{\vec{e}(\vec{q};s,2,1),\vec{e}(\vec{q};s,2,2),\ldots,\vec{e}(\vec{q};s,2,f_{s})\} \\ \vdots \\ \vdots \\ \omega_{sc_{s}}^{2}(\vec{q}) \neq \{\vec{e}(\vec{q};s,c_{s},1),\vec{e}(\vec{q};s,c_{s},2),\ldots,\vec{e}(\vec{q};s,c_{s},f_{s})\} .$$
(C.9)

At this point in the process the so called "compatibility relations" can be examined. Through these relations the changes in the decompositions and degeneracies are determined as \vec{q} moves to a neighboring point \vec{q}' . Such is the case as \vec{q} moves along a line of symmetry to a point on the BZ, \vec{q}' say, where $G_{o}(\vec{q})$ is a subgroup of $G_{o}(\vec{q}')$. The compatibility relations are simply the decompositions of the IMR's of $G_{o}(\vec{q}')$ in terms of the IMR's of $G_{o}(\vec{q})$;

$$\tau^{s}(\vec{q}') = \sum c_{q} \tau^{\sigma}(\vec{q})$$
 (C.10)

where the sum is over the IMR's of $G_{o}(\vec{q})$ and are obtained in the usual way by using Equation (C.6). The application of the compatibility relations will be examined in the context of the bcc and hcp examples.

Construction of symmetry-adapted vectors

In order to construct the symmetry-adapted vectors the projection operator $P^{s}_{\lambda\lambda}(q)$ is created from the definition

$$P_{\lambda\lambda}^{s}(\vec{q}) = \frac{f_{s}}{h} \sum_{\underline{R} \in G_{o}} [\tau_{\lambda\lambda}^{s}(\vec{q};\underline{R})] * \underline{T}(\vec{q};\underline{R}) . \qquad (C.11)$$

By operating on each member of the set of 3n component unit vectors

where $\vec{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$, $\vec{e}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ and $\vec{e}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$, one projects out c_s mutually

orthogonal vectors. In practice one simply examines the 3n columns of $P_{\lambda\lambda}^{s}(\vec{q})$ to obtain the c_s vectors which are labeled $\varepsilon(\vec{q};s,l,\lambda)$, $\varepsilon(\vec{q};s,2,\lambda)$, ..., $\varepsilon(\vec{q};s,c_{s},\lambda)$. Corresponding to each of these vectors are $(f_{s}-1)$ partners which are obtained using the operators

$$P_{\mu\lambda}^{s}(\vec{q}) = \frac{f_{s}}{h} \sum_{\underline{R} \in G_{o}} [\tau_{\mu\lambda}^{s}(\vec{q};\underline{R})] * \underline{T}(\vec{q};\underline{R}) , \qquad (C.13)$$

where $\mu=1,2,\ldots,f_s$ and $\mu\neq\lambda$. Thus, c_s or the normal sets, corresponding to the c_s occurrences of $\tau^{s}(\vec{q})$ in $T(\vec{q})$, can be formed as follows

$$\{\vec{e}(\vec{q}; s, 1, 1), \vec{e}(\vec{q}; s, 1, 2), \dots, \vec{e}(\vec{q}; s, 1, f_{s})\},$$

$$\{\vec{e}(\vec{q}; s, 2, 1), \vec{e}(\vec{q}; s, 2, 2), \dots, \vec{e}(\vec{q}; s, 2, f_{s})\},$$

$$\{\vec{e}(\vec{q}; s, c_{s}, 1), \vec{e}(\vec{q}; s, c_{s}, 2), \dots, \vec{e}(\vec{q}; s, c_{s}, f_{s})\},$$

$$(C.14)$$

By obtaining such a set of vectors corresponding to each $\tau^{s}(\vec{q})$ in the decomposition of $T(\vec{q})$, a set of 3n (by Equation (C.8)) symmetry-adapted vectors $\{\vec{\epsilon}'(\vec{q})\}$ is constructed.

Block diagonalizing $\underline{D}(\vec{q})$

Each symmetry-adapted vector $\vec{\epsilon}(\vec{q} s,a,\lambda) \epsilon \{\vec{\epsilon}(\vec{q})\}$ obeys the relation

$$\vec{\epsilon}(\vec{q};s;a;\lambda')^{\dagger} \underline{D}(\vec{q})\vec{\epsilon}(\vec{q};s,a,\lambda) = \delta_{ss}'\delta_{\lambda\lambda}'$$
(C.15)

Thus, if the matrix $\underline{\Sigma}(\vec{q})$ is formed from $\{\vec{\epsilon}(\vec{q})\}$ by arranging the vectors as follows

$$\{\dots, \vec{e}(\vec{q}; s, 1, 1), \vec{e}(\vec{q}; s, 2, 1), \dots, \vec{e}(\vec{q}; s, c_{s}, 1) ,$$

$$\vec{e}(\vec{q}; s, 1, 2), \vec{e}(\vec{q}; s, w, w), \dots, \vec{e}(\vec{q}; s, c_{s}, 2) ,$$

$$\vec{e}(\vec{q}; s, 1, f_{s}), \vec{e}(\vec{q}; s, 2, f_{s}), \dots, \vec{e}(\vec{q}; s, c_{s}, f_{s}), \dots\} ,$$
 (C.15)

then $\underline{\Sigma}(\vec{q})$ block diagonalizes $\underline{D}(\vec{q})$ via

$$\underline{D}(\vec{q}) = \underline{\Sigma}(q)^{\dagger}\underline{D}(\vec{q})\underline{\Sigma}(\vec{q}) \quad . \tag{C.16}$$

The form of the matrix $\underline{D}(\vec{q})$ is that of f_s blocks of dimension $c_s \times c_s$ lying on the diagonal of the matrix. (The dynamical matrix may first be simplified using the relation

$$\underline{D}(\vec{q}) = \underline{T}(\vec{q};\underline{R})\underline{D}(\vec{q})\underline{T}^{\dagger}(\vec{q};\underline{R}) , \qquad (C.17)$$

before it is block diagonalized.)

Application of Group Theoretical Techniques to the bcc Crystal

The space group of the bcc lattice is 0_h^9 with corresponding point group 0_h of order h=48. Half of the 48 operations of 0_h are proper rotations and are defined in Table 12 with respect to Figure 46. The 3 by 3 matrix representations, the <u>R</u> matrices, for these operations are given in Table 13. The remaining 24 operations of 0_h are improper rotations and are merely the 24 proper rotations followed by the inversion operation 1.

Operation	Defined as
E	Identity
C(3α),C(3β),C(3γ),C(3δ)	120° rotation about 0α , 0β , 0γ and 0δ respectively in the right hand sense
C(3α) ⁻¹ ,C(3β) ⁻¹ ,C(3γ) ⁻¹ ,C(3δ) ⁻¹	Inverse operations of C(3 α), C(3 β), C(3 γ) and C(3 δ) respectively
C(2x),C(2y),C(2z),C(2a),C(2b), C(2c),C(2d),C(2e),C(2f)	180° rotation about 0x, 0y, 0z, 0a, 0b, 0c, 0d, 0e and 0f respectively
C(4x),C(4y),Ç(4z)	90° rotation about 0x, 0y and 0z respectively
C(4x) ⁻¹ ,C(4y) ⁻¹ ,C(4z) ⁻¹	Inverse operations of C(4x), C(4y) and C(4z) respectively

Table 12. Proper rotations of the point group 0_h (refer to Figure 46)

+ ×,γ,z))	= <u>د</u> (4	3,γ,δ) , <u>c</u> (4×,γz) ⁻¹	$(\underline{\mathbf{C}}(3\alpha,\beta,\gamma,\delta)^{-1} = \underline{\tilde{\mathbf{C}}}(3\alpha,\beta)$
	= -1 0	<u>c</u> (2f)	
		<u>C</u> (2e)	$\underline{C}(2z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
	= 0 0	<u>c</u> (2d)	$\underline{C}(2y) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 - 1 \end{pmatrix}$
0	= 0 0	<u>C</u> (2c)	$\underline{C}(2x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
		<u>с</u> (2ь)	$\underline{C}(3\delta) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$
	=	<u>c</u> (2a)	$\underline{C}(3\gamma) = \begin{pmatrix} 0-1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$
-00		<u>C</u> (4z) :	$\underline{\mathbf{C}}(3\beta) = \begin{pmatrix} 0 - 1 & 0 \\ 0 & 0 - 1 \\ 1 & 0 & 0 \end{pmatrix}$
	=	<u>c</u> (4γ) -	$\underline{\mathbf{C}}(3\alpha) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$
0-0	=	<u>c</u> (4 _x) -	$\underline{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

ł

Table 13. Matrices for the 24 proper rotations of $\mathbf{0}_{h}$ for the bcc crystal (see Figure 47)

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Figure 47. Axes of rotation for the symmetry operations of 0_h

For example, the operation which is the reflection in the x-y plane is IC(2z) or

$$\underline{\mathrm{IC}}(2z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

where

$$\underline{I} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{and} \quad \underline{C}(2z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The Brilloun zone for the bcc lattice is shown in Figure 42 with special symmetry points and lines indicated. The point group of the wave vector $G_0(\vec{q})$ for \vec{q} at these points and along these lines is given in Table 14. Also given in Table 14 are the elements of each point group separated according to classes C₁.

The simplifications that can be made in this situation make the problem for the bcc lattice a trivial one. Since the lattice is bravais, n=1 and k takes on only one value. If we chose $\vec{x}(k)=0$ then the $\underline{T}(\vec{q};\underline{R})$ of Equation (C.3) are simply $\underline{T}(\vec{q};\underline{R})=\underline{R}$, the 3x3 matrices of Table 13. Thus the IMR's and the ordinary IR's are the same. This is why the IR's of Cornwell (69) can be used.

The calculations will be demonstrated for \vec{q} along Δ , \vec{q} =(0,0, ζ), and the results listed for other values of \vec{q} . From Table 14 there are eight elements in the point group $G_0(\vec{q})=C_{4v}$ for \vec{q} along Δ and they form the following five classes

$$C_1 = E$$
, $C_4 = IC(2x), IC(2y)$,
 $C_2 = C(2z)$, $C_5 = IC(2a), IC(2b)$.
 $C_3 = C(4z), C(4z)^{-1}$,

Point (q)	Coordinate	G _o (q)	Elements
Г	(000)	0 _h	All 48 operations
Н	2π/a(001)	0 _h	All 48 operations
N	2π/a(½½0)	^D 2h	C ₁ to C ₈ ; E, C(2z,a,b), 1, IC(2z,ab), respectively
Ρ	2π/a(<u>½½</u>)	т _d	C ₁ =E, C ₂ =C(3α,β,γ,δ) ^{±1} , C ₃ =C(2x,y,z), C ₄ =IC(4x,y,z) ^{±1} , C ₅ =IC(2a,b,c,d,e,f)
Line	Coordinate 0<ç<1	G _o (q)	Elements
∆(Γ to H)	π / a(002ζ)	c _{4v}	$C_1 = E$, $C_2 = C(2z)$, $C_3 = C(4z)^{\pm 1}$, $C_4 = IC(2x,y)$, $C_5 = IC(2a,b)$
Λ(Γ to P)	π /a(ζζζ)	c _{3v}	$C_1 = E, C_2 = C(3\delta)^{\pm 1}, C_3 = IC(2b,d,f)$
$\Sigma(\Gamma to N)$	π/a(ζζ0)	c _{2v}	C ₁ =E, C ₂ =C(2a), C ₃ =IC(2z), C ₄ =IC(2b)
G(H to N)	π /a(ζζ ι)	c _{2v}	$C_1=E, C_2=C(2b), C_3=IC(2z), C_4=IC(2a)$
D(N to P)	π/a(½ ½ζ)	c _{2v}	$C_1=E, C_2=C(2z), C_3=IC(2a), C_4=IC(2b)$
F(H to P)	π/a(l-ζ,l-ζ, l+ζ)	c _{3v}	$C_1 = E, C_2 = C(3\alpha)^{\pm 1}, C_3 = IC(2b, c, e)$

Table 14. Point group of the wave vector, $G_{0}(\vec{q})$ for \vec{q} at the points and lines of high symmetry in the reciprocal space of the bcc crystal (69)

The character table for $G_0(\vec{q})$ is given in Table 15 with the $\tau^{S}(\vec{q})$ denoted Δ_{s} . Using Equation (C.6)

$$c_{s} = \frac{1}{h} \sum_{\underline{R} \in G_{O}} [\chi^{s}(\underline{q};\underline{R})] * \chi(\underline{q};\underline{R}) ,$$

the characters from Table 15 and the matrices in Table 13 we obtain

$$c_{\Delta 1} = \frac{1}{8} [3 - 1 + (1)2 + (1)2] = 1$$

$$c_{\Delta 2} = \frac{1}{8} [3 - 1 + (-1)2 + (1)2 + (-1)2] = 0$$

$$c_{\Delta 1} = \frac{1}{8} [3 - 1 + (1)2 + (-1)2 + (-1)2] = 0$$

$$c_{\Delta 2} = \frac{1}{8} [3 - 1 + (-1)2 + (-1)2 + (1)2] = 0$$

$$c_{\Delta 5} = \frac{1}{8} [(2)3 + (-2)(-1) + (0)2 + (0)2] = 1$$

Thereby the decomposition of $T(\Delta)$ is obtained as

$$T(\Delta) = \Delta_1 + \Delta_5$$

where Δ_1 and Δ_5 are one and two dimensional IR's respectively with $f_1=1$ and $f_5=2$ respectively. (The dimensionality of an IR is apparent from the character table since)

$$\chi^{s}(\vec{q};E) = \operatorname{Tr} \underline{\tau}^{s}(\vec{q};E) = f_{s} \qquad (C.19)$$

Also, it can be seen that Equation (C.8) is satisfied with the above values for c_s , f_s and n.

The symmetry-adapted vectors may now be deduced for the IR's in the decomposition by using the projection operator technique of Equation (C.II)

$$P_{\lambda\lambda}^{s}(\vec{q}) = \frac{t_{s}}{h} \sum_{\underline{R} \in G_{o}} [\tau_{\lambda\lambda}^{s}(\vec{q};\underline{R})] * \underline{T}(\vec{q};R) . \qquad (C.20)$$

	Cl	C ₂	C ₃	C4	C ₅	
Δ1	ı	1	1	1	1	
Δ ₂	1	1	-1	1	-1	
Δ1'	1	1	1	-1	-1	
Δ ₂ '	1	1	-1	-1	1	
Δ ₅	2	-2	0	0	0	
$\underline{\tau}^{5}(\Delta, E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ $\underline{\tau}^{5}(\Delta, C(4z)) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$			<u>τ</u> ⁵ (Δ,C <u>τ</u> ⁵ (Δ,C	$\frac{\tau^{5}(\Delta, C(2z)) = \begin{pmatrix} -1 & 0 \\ \cdot & 0 - 1 \end{pmatrix}}{\underline{\tau}^{5}(\Delta, C(4z)^{-1}) = \begin{pmatrix} 0 - 1 \\ 1 & 0 \end{pmatrix}}$		
$\underline{\tau}^{5}(\Delta, C(2x)) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$			$\underline{\tau}^{5}(\Delta, IC(2\gamma)) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$			
$\underline{\tau}^{5}(\Delta, C(2a)) = \binom{0-1}{-1}$			$\tau^5(\Delta, I)$	$\underline{\tau}^{5}(\Delta, C(2b)) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$		

Table 15. Character table for the point group G $(\vec{q})=C_4$ for \vec{q} along Δ in the bcc crystal and matrices for the two dimensional irreducible representation Δ_5 (69)

For Δ_1 we have

$$P_{1}^{1}(\Delta) = \frac{1}{8} [\underline{E} + \underline{C}(2z) + \underline{C}(4z) + \underline{C}(4z)^{-1} + \underline{IC}(2x) + \underline{IC}(2y) + \underline{IC}(2a) + \underline{IC}(2b)] = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
(C.21)

which in turn gives the symmetry-adapted vector

$$\vec{\epsilon}(\Delta;1,1,1) = \vec{e}_3 = \begin{pmatrix} 0\\0\\1 \end{pmatrix}$$
.

For ${\rm \Delta}_5$ we use the matrices for ${\rm \Delta}_5$ from Table 15 to obtain

$$P_{11}^{5}(\Delta) = \frac{2}{8} [(1)\underline{E} + (-1)\underline{C}(2z) + (0)\underline{C}(4z) + (0)\underline{C}(4z)^{-1} + (-1)\underline{IC}(2x) + (1)\underline{IC}(2y) + (0)\underline{IC}(2a) + (0)\underline{IC}(2b)] = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(C.22)

and
$$P_{22}^{5}(\Delta) = \frac{2}{8} [(1)\underline{E} + (-)\underline{C}(2z) + (0)\underline{C}(4z) + (0)\underline{C}(4z)^{-1} + (1)\underline{IC}(2x) + (-1)\underline{IC}(2y) + (0)\underline{IC}(2a) + (0)\underline{IC}(2b)] = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
 (C.23)

The corresponding symmetry-adapted vectors are

$$\vec{\epsilon}(\Delta;5,1,1) = \vec{e}_1 = \begin{pmatrix} 1\\0\\0 \end{pmatrix}$$
 and $\vec{\epsilon}(\Delta;5,1,2) = \vec{e}_2 = \begin{pmatrix} 0\\1\\0 \end{pmatrix}$. (C.24)

Summarizing the results so far for $\boldsymbol{\Delta}$ we have

$$T(\Delta) = \Delta_1 + \Delta_5 \quad \vec{\epsilon}(\Delta_1, L) = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \vec{\epsilon}(\Delta_5, T) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{\epsilon}(\Delta_5, T') = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad (C.25)$$

(The meaning of the L, T and T' indices will be made clear shortly.) The physical interpretation of these results is that along Δ , \vec{q} in the [001] direction, there are two dispersion branches (both acoustic, of course, since n=1) with one being doubly degenerate. The symmetry-adapted vector or polarization vector for the Δ_1 branch indicates that this is the longitudinal branch with polarization vector (Δ_1 ,L). Similarly the symmetry-adapted vectors for the degenerate Δ_5 branches indicate that they are transverse with polarization vectors $\vec{\epsilon}(\Delta_5,T)$ and $\vec{\epsilon}(\Delta_5,T^{\dagger})$.

The decompositions and symmetry-adapted vectors for \vec{q} along the symmetry directions are contained in Tables 16 and 17. Table 16 gives the decompositions for all symmetry points and lines as given in Table 14 and also the compatibility relations in going from a symmetry line to a symmetry point.

Using the matrices $E(\vec{q})$ formed by the symmetry-adapted vectors, the dynamical matrix can be diagonalized for \vec{q} in the symmetry directions. First though, $D(\vec{q})$ is simplified through the use of Equation (C.17) which is a process similar to that of reducing the number of independent element in the force constant matrices (see Appendix D). Let us consider $\underline{D}(\vec{q}) = \underline{D}(\Delta)$ ($\vec{q} = (00\zeta)$) as an example. The elements of the point group $G_O(\Delta) = C_{4V}$, with respect to which $\underline{D}(\Delta)$ is invariant are given in Table 14. It is sufficient to employ only $\underline{C}(4z)$ and $\underline{IC}(2x)$, two elements of $G_O(\Delta)$ which can be used to generate all other elements of the group. For the elements $\underline{R} \in G_O(\Delta)$ it is true that

$$\underline{D}(\vec{q}) = \underline{R} \ D(\vec{q}) \underline{R}$$
(C.26)

from the corresponding relation for the force constant matrices of

Equation (1.20). Then we must have for $\underline{R} = \underline{IC}(2x)$

$$\frac{1C(2x)}{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}} \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix} (C.28)$$

$$\begin{pmatrix} D_{11}^{-D} D_{12}^{-D} D_{13} \\ -D_{21} & D_{22} & D_{23} \\ -D_{31} & D_{32} & D_{33} \end{pmatrix} =$$

which means that

or

$$D_{12} = -D_{12} = 0$$

 $D_{13} = -D_{13} = 0$
 $D_{21} = -D_{12} = 0$
 $D_{31} = -D_{31} = 0$ (C.29)

and therefore

$$\underline{\mathbf{D}}(\Delta) = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{D}_{22} & \mathbf{D}_{23} \\ \mathbf{0} & \mathbf{D}_{32} & \mathbf{D}_{33} \end{pmatrix}$$
(C.30)

Letting $\underline{R} = \underline{C}(4z)$ $\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & D_{23} \\ 0 & D_{32} & D_{33} \end{pmatrix} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & D_{23} \\ 0 & D_{32} & D_{33} \end{pmatrix}$ $\begin{pmatrix} D_{22} & 0 & D_{23} \\ 0 & D_{11} & 0 \\ D_{32} & 0 & D_{33} \end{pmatrix} =$ (C.31)

which means that

$$D_{23} = D_{32} = 0$$
 and $D_{11} = D_{12}$ (C.32)

and therefore

$$\underline{D}(\Delta) = \begin{pmatrix} D_{11} & 0 & 0 \\ 0 & D_{11} & 0 \\ 0 & 0 & D_{33} \end{pmatrix}$$
(C.33)

Writing the equations of motion in matrix form

$$m\omega_{\xi}^{2}(\Delta) \quad \vec{\epsilon}(\Delta; \xi) = \underline{D}(\Delta) \quad \vec{\epsilon}(\Delta; \xi)$$
 (C.34)

by using Equation (1.28) and the unitless eigenvectors or polarization vectors (Equation (1.37)), and using the polarization vectors of Equation (C.25) the $\omega_{\xi}^{2}(\Delta)$ in terms of the D_{ii}(Δ) may be determined. For example

١

$$m\omega_{L}^{2}(\Delta) \stackrel{\stackrel{\rightarrow}{\epsilon}}{\epsilon}(\Delta_{1},L) = \underline{D}(\Delta) \stackrel{\stackrel{\rightarrow}{\epsilon}}{\epsilon}(\Delta_{1},L)$$
(C.35a)

which becomes by substitution

$$m\omega_{L}^{2}(\Delta)\begin{pmatrix}0\\0\\1\end{pmatrix} = \begin{pmatrix}D_{11} & 0 & 0\\0 & D_{11} & 0\\0 & 0 & D_{33}\end{pmatrix} \begin{pmatrix}0\\0\\1\end{pmatrix} , \qquad (C.35b)$$
$$m\omega_{L}^{2}(\Delta_{1}) = D_{33} . \qquad (C.35c)$$

(C.35c)

or

Similarly, we may obtain

$$m\omega_T^2(\Delta_5) = D_{11}$$
, (C.36a)

and

$$m\omega_T^2$$
, $(\Delta_5) = D_{11}$ (C.36b)

The final piece of information for phonons with \vec{q} along Δ comes at the endpoints of Δ ; Γ and H. By transforming $\underline{D}(\Delta)$ with $C(3\alpha) \in G_{O}(\Gamma) =$ $G_{(H)}$ we find that

$$D_{11} = D_{33}$$
 (C.37)

Through this determination we see exactly how the longitudinal and transverse branches become degenerate at Γ and H for $\dot{q} = \frac{\pi}{a}(00\zeta)$, a fact already evident from the decomposition of $G_O(\Gamma)$ and $G_O(H)$ (see Table 16). A summary of the above results and similar results along Σ , Λ , F, D and G are found in Table 17.

The group theoretical analysis for the bcc crystal and in particular the $[00\zeta]\Delta$ direction is so trivial that much of the full power of the technique is not brought to bear. For example $\underline{D}(\Delta)$ was already diagonalized after being brought into symmetrized form and the process of Equation (C.16) was not needed to diagonalize it. In order to demonstrate this process consider the $[\zeta, \zeta, 0]\Sigma$ direction. Using the elements $\underline{C}(2a)$ and $\underline{1C}(2z)$ of the point group C_{2v} for Σ and applying Equation (C.26), $\underline{D}(\Sigma)$ becomes

$$\underline{\mathbf{D}}(\Sigma) = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \mathbf{0} \\ \mathbf{D}_{12} & \mathbf{D}_{11} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{D}_{33} \end{pmatrix}$$
(C.38)

As was done for Δ , Equation (C.34) could be used to find $\omega_{\xi}^{2}(\Sigma)$ as a function of $D_{ij}(\Sigma)$ but for demonstration purposes let us use the process of Equation (C.16). Using the polarization (symmetry-adapted) vectors for Σ given in Table 17, the transformation matrix is formed

$$\underline{\Sigma}(\Sigma) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix}$$
(C.39)

where columns one through three correspond to the L, ${\rm T}_1$ and ${\rm T}_2$ modes respectively.

Transforming $\underline{D}(\Sigma)$ by Equation (C.16) we find

$$\underline{\mathbf{D}}'(\Sigma) = \underline{\Sigma}^{\dagger}(\Sigma) \ \underline{\mathbf{D}}(\Sigma) \ \underline{\Sigma}(\Sigma)$$
(C.40a)

		والمراجع والمستجد فالمستجد والمستجد والمتحد والمتحد والمتحد والمحاد والمحاد والمحاد والمحاد والمحاد والمحاد وال
[00 ζ]∆	$T(\Delta) = \Delta_1 + \Delta_5$	$\Gamma_{15} \rightarrow \Delta_1 \Delta_5$
[ζζ 0] Σ	$T(\Sigma) = \Sigma_1 + \Sigma_3 + \Sigma_4$	Σ ₁ Σ ₃ Σ ₄ Λ ₁ Λ ₃
[ζζζ]Λ	$T(\Lambda) = \Lambda_1 + \Lambda_3$	$H_{15} \rightarrow \Delta_1 \Delta_5$
ענידו	$T(D) = D_{1} \pm D_{2} \pm D_{3}$	$F_1 \Gamma_3$
7 <u>55</u> 27D	1(0) - 01+03+04	616364
[ζζ 1] G	$T(G) = G_1 + G_3 + G_4$	$P_4 \rightarrow \Lambda_1 \Lambda_3$ F_1F_3
[ζζζ]F	$T(F) = F_1 + F_3$	$D_1 D_3 D_4$
[000] Г	$T(\Gamma) = \Gamma_{15}$	$N_1' \rightarrow \Sigma_1$
Гоолан	$T(H) = H_{15}$	$\begin{array}{c} N_{4}^{+} \rightarrow \Sigma_{4} \\ N_{2}^{+} \rightarrow \Sigma_{2} \end{array}$
		·· ·j . — j
L <u>5</u> 57]b	$T(P) = P_{4}$	N ₁ ' → D ₃ N ₄ ' → D ₄
[1 70]N	$T(N) = N_1' + N_4' + N_3'$	$N_3' \rightarrow D_1$
		$N_1' \rightarrow G_4$
		N ₄ ' → G ₁ N ₃ ' → G ₃

Table 16. Decompositions and compatibility relations for lines and points of high symmetry in the bcc crystal
$\begin{bmatrix} 00\zeta \end{bmatrix} \Delta \qquad G_{\Omega}(\Delta) = C_{4\gamma}$ Generators; C(4z), IC(2x) $\underline{\mathbf{D}}^{\mathsf{I}}(\Delta) = \begin{pmatrix} \mathsf{D}_{11} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathsf{D}_{11} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathsf{D}_{22} \end{pmatrix}$ $\underline{\mathbf{D}}(\Delta) = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{D}_{11} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{D}_{23} \end{pmatrix}$ $m\omega_1^2(\Delta_1) = D_{33}$ $m\omega_{\rm L}^{(\Delta_1)} = 0$ $m\omega_{\rm T}^2(\Delta_5) = D_{11} \qquad \overrightarrow{\epsilon}(\Delta_1, L) = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad \overrightarrow{\epsilon}(\Delta_5, T) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \overrightarrow{\epsilon}(\Delta_5, T') = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ $m\omega_T^2(\Delta_5) = D_{11}$ at Γ and H; $D_{11} = D_{33}$ (R = C(3 α)) $[\zeta\zeta 0]\Sigma \qquad G_{O}(\Sigma) = C_{2V}$ Generators; C(2a), IC(2z) $\underline{D}'(\Sigma) = \begin{pmatrix} D_{11} + D_{12} & 0 & 0 \\ 0 & D_{11} - D_{12} & 0 \\ 0 & 0 & D_{23} \end{pmatrix}$ $\underline{\mathbf{D}}(\Sigma) = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \mathbf{0} \\ \mathbf{D}_{12} & \mathbf{D}_{11} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{D}_{22} \end{pmatrix}$ $m\omega_{L}^{2}(\Sigma_{1}) \approx D_{11}+D_{12}$ $m\omega_{L}^{2}(\Sigma_{1}) = D_{11} + D_{12}$ $m\omega_{T_{1}}^{2}(\Sigma_{4}) = D_{11} - D_{12} \quad \vec{\epsilon}(\Sigma_{1}, L) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ l\\ 0 \end{pmatrix} \quad \vec{\epsilon}(\Sigma_{4}, T_{1}) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ -l\\ 0 \end{pmatrix} \quad \vec{\epsilon}(\Sigma_{3}, T_{2}) = \begin{pmatrix} 0\\ 0\\ l \end{pmatrix}$ $m\omega_{T_2}^2(\Sigma_3) = D_{33}$ at N; $D(\Sigma) = D(N)$ and at Γ ; $D_{12} = 0$, $D_{11} = D_{33}$ $[\zeta\zeta\zeta]\Lambda,F \quad G_{O}(\Lambda) = G_{O}(F) = C_{3v}$ Generators; $C(3\gamma)$, IC(2b) $\underline{D}'(\Lambda) = \begin{pmatrix} D_{11} - 2D_{12} & 0 & 0 \\ 0 & D_{11} - D_{12} & 0 \\ 0 & 0 & D_{11} - D_{12} \end{pmatrix}$ $\underline{\mathbf{D}}(\Lambda) = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \mathbf{D}_{12} \\ \mathbf{D}_{12} & \mathbf{D}_{11} & \mathbf{D}_{12} \\ \mathbf{D}_{12} & \mathbf{D}_{12} & \mathbf{D}_{11} \end{pmatrix}$ $m\omega_1^2(\Lambda_1) = D_{11}+2D_{12}$ $m\omega_{T}^{2}(\Lambda_{3}) = D_{11} - D_{12} \quad \vec{\epsilon}(\Lambda_{1}, L) = \frac{1}{\sqrt{3}} \begin{pmatrix} 1\\ 1\\ 1\\ 1 \end{pmatrix} \quad \vec{\epsilon}(\Lambda_{3}, T) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ -1\\ 0 \end{pmatrix} \quad \vec{\epsilon}(\Lambda_{3}, T') = \frac{1}{\sqrt{6}} \begin{pmatrix} -1\\ -1\\ 2 \end{pmatrix}$ $m\omega_{T_{1}}^{2}(\Lambda_{3}) = D_{11} - D_{12} \quad \text{at P; } D_{12} = 0 \quad (\underline{R} = \underline{C}(2\mathbf{x}))$

Table 17. Summary of results of the application of group theory to the lattice dynamics of the bcc crystal

 $\begin{bmatrix} \frac{1}{2} \frac{1}{2} \zeta \end{bmatrix} D \qquad G_{O}(D) = C_{2v}$ The information with \vec{q} along D is the same as with \vec{q} along Σ with the following indices interchanged: $\begin{array}{c} \Sigma_{1} \rightarrow D_{3} & (\pi) \\ \Sigma_{4} \rightarrow D_{4} \\ \Sigma_{3} \rightarrow D_{1} & (\Lambda) \end{array} \qquad \begin{pmatrix} \text{The index in parenthesis is the notation} \\ \text{of Woods et al.} & (58) \end{pmatrix}$ as indicated by the compatibility relations (Table 16). $\begin{bmatrix} \zeta, \zeta, 1 \end{bmatrix} G \qquad G_{O}(G) = C_{2v}$ Again the information with \vec{q} along G is the same as with \vec{q} along Σ with the following indices interchanged: $\begin{array}{c} \Sigma_{1} \rightarrow G_{4} & (\pi_{1}) \\ \Sigma_{4} \rightarrow G_{1} \\ \Sigma_{3} \rightarrow G_{3} & (\pi_{2}) \end{array} \qquad \begin{pmatrix} \text{The index in parenthesis is the notation} \\ \text{of Woods et al.} & (58) \end{pmatrix}$ as indicated by the compatibility relations (Table 16).

$$\underline{\underline{p}}^{1}(\Sigma) = \frac{1}{2} \begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix} \begin{pmatrix} D_{11} & D_{12} & 0 \\ D_{12} & D_{11} & 0 \\ 0 & 0 & D_{33} \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix} = \begin{pmatrix} D_{11}^{+}D_{12} & 0 & 0 \\ 0 & D_{11}^{-}D_{12} & 0 \\ 0 & 0 & D_{33} \end{pmatrix}$$
(C.40b)

This process is analogous to a transformation of coordinate systems. That is the new basis vectors (polarization vectors) corresponding to $\underline{D}^{1}(\Sigma)$ are

$$\vec{\varepsilon}'(\Sigma_1, L) = \begin{pmatrix} 1\\0\\0 \end{pmatrix} ,$$

$$\vec{\varepsilon}'(\Sigma_4, T_1) \stackrel{\ell}{=} \begin{pmatrix} 0\\1\\0 \end{pmatrix} ,$$

$$\vec{\varepsilon}'(\Sigma_3, T_2) = \begin{pmatrix} 0\\0\\1 \end{pmatrix} .$$
 (C.41)

and

Thus, from Equations (C.34), (C.40b) and (C.41) the eigenfrequencies are $m\omega_{1}^{2}(\Sigma_{1}) = D_{11} + D_{12}$, $m\omega_{T_1^2}(\Sigma_4) = D_{11} - D_{12}$, (C.42) $m\omega_{T_{2}^{2}(\Sigma_{3})} = D_{33}$

and

Application of Group Theoretical Techniques to the hcp Crystal

The space group of the hcp crystal is D_{6h}^4 (P6₃/mmc) with point group ${}^{D}_{\mbox{6h}}$ of order 24. The space group is nonsymorphic in that 12 operations have a nonprimitive translation v(R) which depends on the choice of origin. There are two common choices for the origin in the hcp crystal. The first is with the origin at $\vec{x}_0 = (000)$ from Figure 44. Then v(R) is given by

$$v(R) = \frac{a}{2\sqrt{3}}\hat{x} + \frac{a}{2}\hat{y} + \frac{c}{2}\hat{z}$$
 (C.42)

$$= \frac{2}{3} \dot{\vec{a}}_{1} + \frac{1}{3} \dot{\vec{a}}_{2} + \frac{c}{2} \dot{\vec{a}}_{3}$$
 (C.43)

and the symmetry of the environment at the origin is D_{3h} . However, the origin is often taken at a point x'_0 (References 67 and 70) midway between two (001) planes and is given by

$$\vec{x}_{0} = \frac{9}{\sqrt{3}}\hat{x} + \frac{1}{4}c\hat{z}$$
 (C.44)

$$= \frac{1}{3} \dot{\vec{a}}_{1} + \frac{-1}{3} \dot{\vec{a}}_{2} + \frac{1}{4} \dot{\vec{a}}_{3} \qquad (C.45)$$

With \vec{x}_{0}^{\prime} as the origin the symmetry environment at the origin is D_{3d}^{\prime} . The choice of origins determines which operations of the space group are associated with the nonprimitive translation. For our purposes here \vec{x}_{0}^{\prime} will be taken as the origin. The operations of the point group D_{6h}^{\prime} referred to Figure 48 are: E; the identity

 C_{6z} , C_{3z} ; rotations of 60° and 120° about the \vec{z} axis (right hand) C_{2x} , C_{2y} , C_{2z} , C_{2A} , C_{2B} , C_{2C} , C_{2D} ; rotations of 180° about 0x, 0y,0z, 0A, 0B, 0C and 0D respectively

The remaining operations are the inverses of C_{6z} and C_{3z} , C_{6z}^{-1} and C_{3z}^{-1} and the improper rotations obtained by multiplying the above proper rotations by the inversion operator 1. For the origin at \vec{x}_{0} the operations E, C_{3z} , C_{3z}^{-1} , C_{2y} , C_{2C} , C_{2D} , IC_{6z} , IC_{6z}^{-1} , IC_{2z} , IC_{2x} , IC_{2A} and IC_{2B} always appear with primitive translations only. Table 18 gives the connection between several sets of notation. The matrices for the proper rotations are given in Table 19.

The point groups of the various symmetry points and lines of hcp reciprocal space are as follows:



Figure 48. Axes of rotation for the symmetry operations of ${}^{\rm D}_{\rm 6h}$

Cornwell (69) (used here)	lyengar <u>et al</u> . (71)	Herring (72)	Kovalev (70)	
E	E	ε	h ₁	
¢ ₆₇	C ₆ (z)	¢6	h ₂	
C _{3z}	C ₃ (z)	δვ	h ₃	
C ₂₇	C ₂ (z)	δ <u>2</u>	h ₄	
C_{37}^{-1}	$C_{3}(z)^{-1}$	δ3 ⁻¹	h ₅	
c_{6z}^{5-1}	$C_{6}(z)^{-1}$	_{δ6} -1	h ₆	
c _{2B}	C ₂ (6)	δ24 '	h ₇	
c _{2C}	C ₂ (3)	δ23''	h ₈	
c _{2x}	C ₂ (4)	δ 2 2'	hg	
c _{2D}	C ₂ (1)	٥24''	h ₁₀	
c _{2A}	C ₂ (5)	δ ₂₃ '	h11	
c _{2v}	C ₂ (2)	^δ 22''	h ₁₂	
-, I	i	i	h ₁₃	
IC _{6z}	S ₆ (z)	σз	h ₁₄	
IC 3z	S ₃ (z)	σ6	h15	
IC _{2z}	σ _h	ρ	h ₁₆	
$1C_{3z}^{-1}$	$S_{3}(z)^{-1}$	σ6 ⁻¹	h ₁₇	
10 _{6z} 1	S ₆ (z) ⁻¹	σ ₃ ⁻¹	h ₁₈	
1C _{2y}	σ _d (4)	ρ2	h19	
IC _{2c}	σ _d (5)	ρз"	h ₂₀	
IC _{2x}	σ _d (2)	ρ2	h ₂₁	
IC _{2D}	σ <mark>ν</mark> (6)	ρμΊ	h ₂₂	
IC _{2A}	σ (3)	Pз'	h ₂₃	
IC _{2B}	σ _v (1)	ρι'	h ₂₄	

Table 18. Various notations for hcp symmetry operations

.

	6h	
$\underline{\mathbf{E}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{pmatrix}$	0 0 1	$\underline{C}_{2y} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
$\underline{C}_{6z} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{1}{2} \\ 0 & 0 \end{pmatrix}$	0 0 1	$\frac{C_{2z}}{(-1)^2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
$\underline{C}_{3z} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} \\ 0 & 0 \end{pmatrix}$		$\underline{C}_{2A} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$
$\underline{C}_{6z}^{-1} = \begin{pmatrix} \frac{1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	0 0	$\underline{C}_{2B} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & -1 \end{pmatrix}$
$\begin{pmatrix} 0 & 0 \\ \frac{-1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$		$\underline{C}_{2C} = \begin{pmatrix} \frac{1}{2} & \frac{-\sqrt{3}}{2} & 0\\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} & 0\\ 0 & 0 & -1 \end{pmatrix}$
$\frac{c}{2 \times 2} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \\ 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix}$	$\underline{C}_{2D} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & \frac{-1}{2} & 0\\ 0 & 0 & -1 \end{pmatrix}$

.

Table 19. Matrices for the symmetry operations for the 12 proper rotations of D_{6h} for the hcp crystal (see Figure 47)

^r ; ^D 6h	s; c _{2v}	τ'; c _{2v}	
∆; ^C 6v	s'; c _{2v}	M; D _{2h}	
∑; c _{2∨}	L; D _{2h}	K; D _{3h}	(C.46)
τ; c _{2v}	H; D _{3h}	P; C _{3v}	
R; C _{2v}	A; ^D 6h	U; C _{2v}	

The elements of these point groups, class composition and character tables are given in Cornwell (69).

The extent of the following discussion will be to deduce the decomposition along Δ as an example with the other decompsitions as well as compatibility relations tabulated only.

The first step in the decomposition process is to obtain the $\underline{T}(\mathbf{q}, \mathbf{R})$ matrices for the elements of the point group of Δ , C_{6v} . The elements and classes of C_{6v} are

primitive translations only nonprimitive translations

The matrices $\underline{T}(\vec{q},\underline{R})$ are obtained from Equation (C.3) with $R_{\alpha\beta}$ being the 3x3 matrices in Table 19 and

$$\delta(k,F(k',R)) = 1 \text{ for } k=k' \text{ and } Classes C_1, C_2, C_3$$

$$k\neq k^i \text{ and } Classes C_4, C_5, C_6,$$

$$= 0 \text{ for } k\neq k' \text{ and } Classes C_1, C_2, C_3$$

$$k=k' \text{ and } Classes C_4, C_5, C_6. \quad (C.48)$$

The exponential factor $\alpha = \exp\{i \ \vec{q} \cdot [\vec{x}(k) - \underline{R}\vec{x}(k^{T})]\}$ are obtained below.

$$\frac{\text{For } \dot{q} \text{ along } \Delta; \ \dot{q} = \frac{2\pi}{c} (0,0,\zeta) (\zeta=0 \text{ to } .5) \text{ thus we need only}$$
consider the z components of $\dot{x}(k)$ for k=1,2 which are
$$x_{z}(k) = 0 \quad \text{for} \quad k=1$$
and
$$x_{z}(k) = \frac{c}{2} \quad \text{for} \quad k=2$$
Classes $C_{1}, C_{2}, C_{3}; \quad k=k^{i} \quad \underline{R}(\dot{x}(k^{i}) = \dot{x}(k^{i}) = x(k) \qquad (C.49)$
and $\alpha=1$

$$k \neq k^{i} \quad \delta(k, F(k^{i}, R)) = 0$$
independently of α
Classes $C_{4}, C_{5}, C_{6}; \quad k=k^{i} \quad \delta(k, F(k^{i}, R)) = 0 \qquad (C.50)$
independently of α

$$k \neq k^{i} \quad k=2, \ k^{i}=1; \ x_{z}(2) = \frac{c}{2}$$

$$(\underline{R}\dot{x}(1))_{z} = 0$$
then $\alpha = \exp(i\tau\zeta)$ for all \underline{R}
in C_{4}, C_{5} or C_{6} . The same
is true for k=1, k'=2.

The matrices $\underline{T}(\overrightarrow{q},\underline{R}) = \underline{T}(\Delta,\underline{R})$ are then

$$\underline{T}(\Delta,\underline{R}) = \begin{pmatrix} \underline{R} & 0 \\ 0 & \underline{R} \end{pmatrix} \quad \text{for } \underline{R} \text{ in } C_1, C_2, C_3, \qquad (C.51)$$

and
$$\underline{T}(\Delta,\underline{R}) = \begin{pmatrix} 0 & \underline{R} \\ \underline{R} & 0 \end{pmatrix} e^{i\pi\xi}$$
 for \underline{R} in C_4 , C_5 , C_6 . (C.52)

We may now use Equation (C.6) together with the character table (Table 20) from Cornwell (69) to find the decomposition along Δ :

	C ₁	C ₂	C 3	C4	C 5	C ₆	
Δ_1	1	1	1	1	1	I	
Δ ₃	1	1	-1	1	1	-1	
Δ_5	2	-1	0	2	-1	0	
Δ ₂	1	1	1	-1	-1	- 1	
Δ4	1	1	-1	-1	-1	ĩ	
Δ ₆	2	-1	0	-2	1	0	

Table 20. Character table for the point group $G_0(\vec{q}) = C_{6v}$ for \vec{q} along Δ in the hcp crystal (69)

$$c_{\Delta 1} = \frac{1}{12} [6 + 6] = 1$$

$$c_{\Delta 2} = \frac{1}{12} [6 + 6] = 1$$

$$c_{\Delta 3} = \frac{1}{12} [6 - 6] = 0$$

$$c_{\Delta 4} = \frac{1}{12} [6 - 6] = 0$$

$$c_{\Delta 5} = \frac{1}{12} [12 + 0] = 1$$

$$c_{\Delta 6} = \frac{1}{12} [12 - 0] = 1$$

Therefore,

$$T(\Delta) = \Delta_1 + \Delta_2 + \Delta_5 + \Delta_6 \qquad (C.54a)$$

.

By similar methods for \overrightarrow{q} along Σ and T we obtain

$$T(\Sigma) = 2\Sigma_1 + 2\Sigma_3 + 2\Sigma_4$$
 (C.54b)

$$T(T) = 2T_1 + T_2 + T_3 + 2T_4$$
 (C.54c)

At the special points $\Gamma,\ K,\ M$ and A we have

$$T(\Gamma) = \Gamma_2 + \Gamma_6 + \Gamma_5^+ + \Gamma_3^+$$
 (C.54d)

$$T(K) = K_1 + K_3 + K_5 + K_6$$
 (C.54e)

$$T(M) = M_1^+ + M_2^- + M_3^+ + M_3^- + M_4^+ + M_4^-$$
(C.54f)

$$T(A) = A_1 + A_3$$
 (C.54g)

The notation for the IR's is that of Warren (67) and it should be pointed out that there exist confusing discrepancies in notation within the literature. For example, K_3 in Warren's work (67) is denoted K_2 in that of Raubenheimer and Gilat (45). The compatibility relations are given at $\Gamma,\ K,\ M$ and A as

at
$$\Gamma$$
; $\Gamma_2^- \leftrightarrow \Delta_1$ Σ_3 T_3
 $\Gamma_3^+ \leftrightarrow \Delta_2$ Σ_3 T_2
 $\Gamma_5^+ \leftrightarrow \Delta_5$ $\Sigma_1 \Sigma_4$ $T_1 T_4$
 $\Gamma_6^- \leftrightarrow \Delta_6$ $\Sigma_1 \Sigma_4$ $T_1 T_4$
at K; $K_1 \leftrightarrow T_1$ P_1
 $K_3 \leftrightarrow T_4$ P_2
 $K_5 \leftrightarrow T_1 T_4$ P_3
 $K_6 \leftrightarrow T_2 T_3$ P_3
at M; $M_1^+ \leftrightarrow T_1$ Σ_1 U_1
 $M_2^- \leftrightarrow T_4$ Σ_1 U_2
 $M_3^+ \leftrightarrow T_2$ Σ_3 U_2
 $M_3^- \leftrightarrow T_1$ Σ_4 U_3
 $M_4^+ \leftrightarrow T_4$ Σ_4 U_4
 $M_4^- \leftrightarrow T_3$ Σ_3 U_1
at A; $A_1 \leftrightarrow \Delta_1 \Delta_2$ $R_1 R_3$
 $A_3 \leftrightarrow \Delta_5 \Delta_6$ $R_1 R_2 R_3 R_4$ (C.55d)

Note that the above columns also give the decompositions for the particular direction or point. Finally the phonon modes associated with the IR's are

	along ∆ [001]	TA LA TO LO	Δ ₅ Δ ₁ Δ ₆ Δ ₂	,	(C.56a)
	along Σ [100]	TA TO LA LO TA ₁₁ TO ₁₁		3	(С.56Ь)
d	along T [110]	TA ₁ TO ₁ LA LO TA ₁₁ TO ₁	T ₃ T ₂ T ₁ T ₄ T ₄ T ₄		(C.56c)

and

APPENDIX D. SYMMETRY REDUCTION OF AFC MATRICES AND COMPOSITION OF INTERPLANAR FORCE CONSTANTS IN TERMS OF AFC'S

The bcc Crystal

The AFC matrices for a bcc crystal will be reduced using Equation (1.12)

$$\Phi_{ij}(\ell k, \ell' k') = \Phi_{ji}(\ell' k', \ell k)$$
(D.1)

and Equation (1.20b)

÷

$$\Phi(\mathsf{LK},\mathsf{L'K'}) = \mathsf{R}\Phi(\mathfrak{k},\mathfrak{k'k'})\mathbf{R} \qquad (D.2)$$

We can first reduce all $\Phi_{ii}(lk, l'k')$ to the form

$$\begin{pmatrix} xx & xy & xz \\ xy & yy & yz \\ xz & yz & zz \end{pmatrix}$$
 (D.3)

by using Equation (D.1) and the fact that the bcc crystal is centrosymmetric (Equation (1.23)). To further simplify the force constant matrices, we must first deduce the symmetry operations, the <u>R</u>'s of Appendix C, which leave the "bond" between the atom of the origin and the nth neighbor invariant or reversed. The eight nearest neighbors for bcc crystals are listed in Table 21 in terms of their positions (components $h_1h_2h_3$ along $\frac{a}{2}\hat{x}$, $\frac{a}{2}\hat{y}$, $\frac{a}{2}\hat{z}$ respectively), number (of nth neighbor) and distance from the origin (see Figure 49).

Consider the first nearest neighbor at 111. The operations which leave the "bond" between 000 and 111 invariant are

E,
$$C(3\delta)^{\pm 1}$$
, $IC(2b)$, $IC(2d)$, $IC(2f)$ (D.4)

and those which leave the bond reversed are

$$I, IC(36)^{\pm 1}, C(2b), C(2d), C(2f)$$
 (D.5)

Neighbor n	Position $h_1h_2h_3$	Number of nth neighbors	Distance to origin (R _u)	R _n /a
1	111	8	√3 a/2	0.87
2	200	6	9	1.00
3	220	12	√2 a	1.41
4	311	24	√11 a/2	1.66
5	222	8	√2 a	1.73
6	400	6	2 a	2.00
7	331	24	√19 a/2	2.18
8	420	24	√5 a	2.24

Table 21. Eight nearest neighbors in a bcc crystal (see Figure 49)



Figure 49. 8 neighbor positions in the bcc lattice

as defined in Appendix C (Table 12). The 3x3 matrices for these operations are also given in Appendix C (Table 13).

Before applying Equation (D.2), the following expression is used to determine the number of independent force constants to expect for a given neighbor. The expression is (73)

$$N = \frac{1}{g} \left\{ \sum_{X} (\underline{R})^2 + \sum_{X} (\underline{R}'^2) \right\}$$
(D.6)

where g is the number of operations which leave the bond invariant or reversed, $\chi(\underline{R})$ is the character of the operation \underline{R} , and \underline{R} and \underline{R}' are the bond invariant and reversal operations respectively. Using the operations (D.4) and (D.5) and the characters from the matrices in Table 13 to evaluate N for the first neighbor we get

$$N = \frac{1}{12} \left[9 + 0 + 0 + 1 + 1 + 1 + 3 + 3 + 3 + 3 + 0 + 0 \right] = 2 \quad (D.7)$$

Therefore, we can expect the matrix (D.3) to be reduced to having only two independent force constants.

To begin the reduction process, we select an operation <u>R</u> from Equation (D.4), <u>IC(2b)</u> for example, and then apply Equation (D.2)

$$\underline{\mathbf{R}} \quad \Phi(111)\underline{\mathbf{\hat{R}}} = \Phi(111) \tag{D.8}$$

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} xx & xy & xz \\ xy & yy & yz \\ xz & yz & zz \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} yy & xy & yz \\ xy & xx & xz \\ yz & xz & zz \end{pmatrix} = \begin{pmatrix} xx & xy & xz \\ xy & yy & yz \\ xz & yz & zz \end{pmatrix}$$
(D.9)

This implies that xx=yy and yz=xz and therefore

$$\Phi(111) = \begin{pmatrix} xx & xy & xz \\ xy & xx & xz \\ xz & xz & zz \end{pmatrix}$$
(D.10)

Let <u>R</u> now be IC(2d) then

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} xx & xy & xz \\ xy & xx & zz \\ xz & xz & zz \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} zz & xz & xz \\ xz & xx & xy \\ xz & xy & xx \end{pmatrix} = \begin{pmatrix} xx & xy & xz \\ xy & xx & xz \\ xz & xz & zz \end{pmatrix}$$
 (D.11)

and we have that xx=zz and xy=xz.

The 1st neighbor force constant matrix is now

or in another notation

$$\Phi(111) = \begin{pmatrix} \alpha_1 & \beta_1 & \beta_1 \\ \beta_1 & \alpha_1 & \beta_1 \\ \beta_1 & \beta_1 & \alpha_1 \end{pmatrix} \qquad (D.13)$$

Since we now have only two independent force constants there is no need to continue the process with other <u>R</u>'s from Equation (D.4). In Table 22 we give for neighbors 1 through 8 the following information:

- (1) invariant operation \underline{R} ,
- (2) reversal operations \underline{R}' ,
- (3) N,
- (4) $\phi(h_1h_2h_3)$.

We may now use these matrices to find the composition of the $\Phi_n(\xi)$ in terms of the AFC's. As an example, we consider the (001) type planes on either side of the origin, the (001) and (00T) planes, and find that they contain eight first neighbor atoms located at $h_1h_2h_3 = \pm 1 \pm 1 \pm 1$. The force constant matrices representing the forces between these atoms and the atom at the origin, $\Phi(h_1h_2h_3)$, are obtained by applying the symmetry operation which takes 111 to $h_1h_2h_3$, to $\Phi(111)$. For example, <u>C</u>(2z) takes 111 to -1 -1 1, therefore

n	(h1h2h3)	"Invariant" operations (<u>R</u>)	"Reversal" operations (<u>R</u> 1)	N	∳(h ₁ h ₂ h	n ₃)
1 5	(111)	E,C(^{±1} (3Y),IC(2b) IC(2d),IC(2f)	ι,ιc _(3γ) C _(2b) ,C _(2d) ,C _(2f)	2	(xx xy xy) xy xx xy xy xy xx)	$ \begin{array}{l} xx = \alpha_1 \\ xy = \beta_1 \end{array} $
2 6	(200)	E,C _(2x) ,C _(4x) IC _(2z) ,IC _(2y) IC _(2f) ,IC _(2e)	I,IC _(2x) ,IC _(4x) C _(2z) ,C _(2y) ,C _(2f) C _(2e)	2	$ \begin{pmatrix} xx & 0 & 0 \\ 0 & yy & 0 \\ 0 & 0 & yy \end{pmatrix} $	$ xx = \alpha_2 yy = \beta_2 $
3	(220)	E,C _{2a} , IC _(2b) ,IC _(2z)	^{I,IC} (2a), ^C (2b) ^{,C} (2z)	3	$\begin{pmatrix} xx & xy & 0 \\ xy & xx & 0 \\ 0 & 0 & zz \end{pmatrix}$	$xx = \alpha_3$ $zz = \beta_3$ $xy = \gamma_3$
4	(311)	E, IC _(2f)	ł,C _(2f)	4	(xx xy xy) xy yy yz xy yz yy)	$xx = \alpha_4$ $yy = \beta_4$ $yz = \gamma_4$ $xy=xz=\delta_4$
7	(331)	E,IC _(2b)	^{1,C} (2b)	4	(xx xy xy) xy yy yz xy yz yy)	$xx = \alpha_7$ $yy=zz=\beta_7$ $yz = \gamma_7$ $xy = \delta_7$
8	(420)	E,IC _(2z)	I,C _(2z)	4	$\begin{pmatrix} xx & xy & 0 \\ xy & yy & 0 \\ 0 & 0 & zz \end{pmatrix}$	$xx = \alpha_8$ $yy = \beta_8$ $zz = \gamma_8$ $xy = \delta_8$

Table 22. AFC matrices and their symmetry operations for eight nearest neighbors in a bcc crystal

Similarly,

$$\Phi(1 - 1 - 1) = \begin{pmatrix} xx - xy - xy \\ -xy & xx & xy \\ -xy & xy & xx \end{pmatrix}$$

$$(D.13c)$$

$$(xx - xy & xy)$$

$$\Phi(-1 \ 1 \ -1) = \begin{pmatrix} x x & xy & xy \\ -xy & xx & -xy \\ xy & -xy & xx \end{pmatrix}$$
(D.13d)

$$\Phi(1 \ 1 \ -1) = \begin{pmatrix} xx & xy & -xy \\ xy & xx & -xy \\ -xy & -xy & xx \end{pmatrix}$$
(D.13e)

$$\Phi(1 - 1 1) = \begin{pmatrix} xx - xy & xy \\ -xy & xx - xy \\ xy & -xy & xx \end{pmatrix}$$
(D.13f)

$$\Phi(-1 \ 1 \ 1) = \begin{pmatrix} xx \ -xy \ -xy \\ -xy \ xx \ xy \\ -xy \ xy \ xx \end{pmatrix}$$
(D.13g)

Summing the $\Phi(h_1h_2h_3)$, Equations (D.13a) through (D.13b), we find the matrix

$$\begin{pmatrix} 8xx & 0 & 0\\ 0 & 8xx & 0\\ 0 & 0 & 8xx \end{pmatrix}$$
 (D.14)

This is the first neighbor, n=1 (first set of planes) contribution to the dynamical matrix. From Appendix C we found that in the $[00\zeta]$ direction, \vec{q} along Δ ,

$$m\omega_{L}^{2} = D_{33}$$
 ,
 $m\omega_{T}^{2} = D_{11}$, (D.15)
 $m\omega_{T'}^{2} = D_{11}$.

By inspection of Equations (D.14) and (D.15) we see that

$$\Phi_{1}(L[00\zeta]) = 8(1xx) + \dots$$

$$\Phi_{1}(T[00\zeta]) = 8(1xx) + \dots$$

$$\Phi_{1}(T[00\zeta]) = 8(1xx) + \dots$$
(D.16)

as indicated in Table 2.

The hcp Crystal

The symmetry reduced AFC matrices to six neighbors for the general tensor model are given in Table 23. Also given is k for each neighbor (see Appendix A), NN, the number of nth neighbors and r_n the distance to the nth neighbor.

The force constants in the MAS model originate from Equation (1.62) for the axially symmetric model:

$$\Phi_{ij} = \Phi_t(\delta_{ij} - \frac{R_i R_j}{R_o^2}) + \Phi_r \frac{R_i R_j}{R_o^2}$$
(D.17)

where ϕ_t is the tangential or bond bending force constant and ϕ_r is the radial or bond stretching force constant. In the rotation of DeWames <u>et</u> <u>al</u>. (22), these are written as

$$\Phi_{t} = C_{B}(s, ij)$$
(D.18)

and
$$\Phi_r = C_t(s,ij)$$
 (D.19)

where the interaction is between the jth atom of the sth shell with the

Neighbor n	 Number of nth neighbors 	Force	constant ma	atrix	Distance from origin
l st	6	$\begin{pmatrix} A_1 \\ \sqrt{3} \\ (A_1 - B_1) \end{pmatrix}$	$\frac{\sqrt{3}}{2}(A_1-B_1)$	√3D ₁ \	$a\sqrt{\left(\frac{1}{2}+\frac{\gamma^2}{2}\right)}$
		√3D1	D	G ₁	`3 4'
2 nd	6	/ a _l	<u>-√3</u> (a ₁ -b ₁)	e1	
k=1		$\begin{pmatrix} \frac{-\sqrt{3}}{2} & (a_1-b_1) \\ & e_1 \end{pmatrix}$	b ₁ √3e ₁	√3e ₁ g ₁	a
3 rd k=2	6	$ \left(\begin{array}{c} A_2\\ O\\ O\\ O \end{array}\right) $	0 B ₂ D ₂	0 D ₂ G ₂	$a\sqrt{\frac{4}{3}+\frac{\gamma^2}{4}}$
4 th k=1	2	(a2 0 0	0 a ₂ 0	0 0 92	c = ya
5 th k=2	12	$\begin{pmatrix} A_3 \\ F_3 \\ E_3 \end{pmatrix}$	F ₃ B ₃ D ₃	$\left(\begin{array}{c} E_{3} \\ D_{3} \\ G_{3} \end{array} \right)$	$a\sqrt{\frac{7}{3}+\frac{\gamma^2}{4}}$
6 th k=1	6	(a3 0 0	0 b ₃ 0	0 0 93)	√ <u>3</u> a

Table 23. Force constant matrices for six nearest neighbors in an hcp crystal (see Figure 50)



Figure 50. 6 neighbor positions in the hcp lattice

·····

ith atom in the cell at the origin. Then with

$$K(s,ij) = C_t(s,ij) - C_B(s,ij)$$
 (D.20)

Equation (0.17) becomes

$$\Phi_{ij} = K(s,ij) \frac{R_i R_j}{R_o^2} + C_B(s,ij)$$
 (D.21)

The modification to the thus far axially symmetric model is to replace C_B by C_{Bx} and C_{Bz} . The MAS force constants to six neighbors are (74)

$$\begin{aligned} &\text{lst } \delta_{1} = K(1,12)/(4+3\gamma^{2}) & 2nd \quad \alpha_{2} = K(1,11) \\ &\varepsilon_{1x} = C_{Bx}(1,12) & \dot{\beta}_{2x} = C_{Bx}(1,11) \\ &\varepsilon_{1z} = C_{Bz}(1,12) & \beta_{2z} = C_{Bz}(1,11) \\ &\varepsilon_{1z} = C_{Bz}(1,12) & \beta_{2z} = C_{Bz}(1,11) \\ &\delta_{3} = K(2,12)/(16+3\gamma^{2}) & 4th \quad \alpha_{4} = K(2,11) \\ &\varepsilon_{3x} = C_{Bx}(2,12) & \beta_{4x} = C_{Bx}(2,11) & (D.22) \\ &\varepsilon_{3z} = C_{Bz}(2,12) & \beta_{4z} = C_{Bz}(2,11) \\ &\varepsilon_{5z} = C_{Bz}(2,12) & \delta_{5z} = C_{Bz}(3,12) \\ &\varepsilon_{5z} = C_{Bz}(3,12) & \beta_{6x} = C_{Bz}(3,11) \\ &\varepsilon_{5z} = C_{Bz}(3,12) & \beta_{6z} = C_{Bz}(3,11) \end{aligned}$$

The MAS force constants are related to the general tensor force constants of Table 22 by the following relations (74)

$$A_{1} = \varepsilon_{1x} + 3\delta_{1} , \qquad A_{2} = \varepsilon_{3x} , \qquad A_{3} = \varepsilon_{5x} + 12_{\delta 5} ,$$

$$B_{1} = \varepsilon_{1x} + \delta_{1} , \qquad B_{2} = \varepsilon_{3x} + 16\delta_{3} , \qquad B_{3} = \varepsilon_{5x} + 16\delta_{5} ,$$

$$G_{1} = \varepsilon_{1z} + 3\gamma^{2}\delta_{1} , \qquad G_{2} = \varepsilon_{3z} + 3\gamma^{2}\delta_{3} , \qquad G_{3} = \varepsilon_{5z} + 3\gamma^{2}\delta_{5} ,$$

$$F_{1} = \sqrt{3} \delta_{1} , \qquad F_{2} = 0 , \qquad F_{3} = 8\sqrt{3} \delta_{5} ,$$

$$E_{1} = 3\gamma\delta_{1} , E_{2} = 0 , E_{3} = 6\gamma\delta_{5} , (D.23)$$

$$D_{1} = \sqrt{3}\gamma\delta_{1} , D_{2} = 4\sqrt{3}\gamma\delta_{3} , D_{3} = 4\sqrt{3}\gamma\delta_{5}$$

$$a_{1} = 4\alpha_{2}+\beta_{2x} , a_{2} = \beta_{4x} , a_{3} = \beta_{6x} ,$$

$$b_{1} = \frac{3}{4}\alpha_{2}+\beta_{2x} , b_{2} = \beta_{4x} , b_{3} = \alpha_{6} + \beta_{6x} ,$$

$$g_{1} = \beta_{2z} , g_{2} = \alpha_{4} + \beta_{4z} , g_{3} = \beta_{6z} ,$$

$$f_{1} = \frac{\sqrt{3}}{4}\alpha_{2} , f_{2} = 0 , f_{3} = 0 ,$$

$$e_{1} = 0 , e_{2} = 0 , e_{3} = 0 ,$$

$$d_{1} = 0 , d_{2} = 0 , d_{3} = 0 .$$

The constraints on the general tensor AFC's from these relations are (74)

$$D_{1} = \frac{\sqrt{3}}{2} \gamma (A_{1} - B_{1}) , \qquad D_{2} = \frac{-\sqrt{3}}{4} \gamma (A_{2} - B_{2}) ,$$

$$D_{3} = -\sqrt{3} \gamma (A_{3} - B_{3}) , \qquad E_{3} = \frac{-3}{2} \gamma (A_{3} - B_{3}) ,$$

$$F_{3} = -2\sqrt{3} (A_{3} - B_{3}) . \qquad (D.24)$$

The constraints imposed by the elastic constants are given in terms of the MAS force constants by (42)

$$C_{11} = \frac{4}{C\sqrt{3}} \{ (9/8)_{\alpha_{2}} + (27/8)_{\alpha_{6}} + \frac{3}{2}\delta_{1} + 24\delta_{3} + 147\delta_{5} + \frac{3}{2}\beta_{2x} + \frac{9}{2}\beta_{6x} + \frac{1}{2}\varepsilon_{1x} + 2\varepsilon_{3x} + 7\varepsilon_{5x} - (12/m\omega_{a}^{2})(8\delta_{3}-\delta_{1}-20\delta_{5})^{2} \} ,$$

$$C_{11}-C_{12} = \frac{8}{C\sqrt{3}} \{ (3/8)_{\alpha_{2}} + (9/8)_{\alpha_{6}} + \frac{1}{2}\delta_{1} + 8\delta_{3} + 498_{5} + \frac{3}{2}\beta_{2x} + \frac{9}{2}\beta_{6x} + \frac{1}{2}\varepsilon_{1x} + 2\varepsilon_{3x} + 7\varepsilon_{5x} - (12/m\omega_{a}^{2})(8\delta_{3}-\delta_{1}-20\delta_{5}) = 2C_{66} ,$$

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$$\begin{aligned} c_{44} &= \frac{4\gamma^2}{C\sqrt{3}} \{\frac{3}{2}\delta_1 + 6\delta_3 + 21\delta_5 + \beta_{4x} + \frac{3}{4}\epsilon_{1x} + \frac{3}{4}\epsilon_{3x} + \frac{3}{2}\epsilon_{5x}\}, \\ c_{12} + c_{11} &= \frac{8}{C\sqrt{3}} \{\frac{3}{4}\alpha_2 + \frac{9}{4}\alpha_6 + \delta_1 + 16\delta_3 + 98\delta_5\}, \\ c_{13} + c_{44} &= \frac{4\gamma^2}{C\sqrt{3}} \{3\delta_1 + 12\delta_3 + 42\delta_5\}, \\ c_{44} &= \frac{4}{C\sqrt{3}} \{\frac{3}{2}\gamma^2\delta_1 + 6\gamma^2\delta_3 + 21\gamma^2\delta_5 + \frac{3}{2}\beta_{2z} + \frac{9}{2}\beta_{6z} + \frac{1}{2}\epsilon_{1z} + 2\epsilon_{3z} + 7\epsilon_{5z}\}, \\ c_{33} &= \frac{4\gamma^2}{C\sqrt{3}} \{\alpha_4 + \frac{9}{4}\gamma^2\delta_1 + \frac{9}{4}\gamma^2\delta_3 + \frac{9}{2}\gamma^2\delta_5 + \beta_{4z} + \frac{3}{4}\epsilon_{1z} + \frac{3}{4}\epsilon_{3z} + \frac{3}{2}\epsilon_{5z}\}. \end{aligned}$$

$$(d.25)$$

Using these relations it can be shown (22) that

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$$c\sqrt{3}(c_{44}-c_{13}) = 8\gamma^2 \{\beta_{4x} + \frac{3}{4}\epsilon_{1x} + \frac{3}{4}\epsilon_{3x} + \frac{3}{2}\epsilon_{5x}\}$$
 (D.26)

Thus, if the bond bending force constants β and ε are not included in the model the Cauchy relation $C_{13}=C_{44}$ is obtained. The elastic constraints in terms of the general tensor AFC's are (74)

$$C_{11} = \frac{1}{2\sqrt{3}C} \{12b_{1} + 9(a_{3}+3b_{3}) + 3b_{3} + 4A_{1} + 4(A_{2}+3B_{2}) + 26A_{3} + 30B_{3} + 16\sqrt{3}F_{3} - P\},$$

$$C_{66} = \frac{1}{2\sqrt{3}C} \{12a_{1} + 9(3a_{3}+b_{3}) + 4B_{1} + 4(3A_{2}+B_{2}) + 30A_{3} + 26B_{3} - 16\sqrt{3}F_{3} - P\},$$

$$C_{33} = \frac{C}{\sqrt{3}a^{2}} \{4g_{2} + 3G_{1} + 3G_{2} + 6G_{3}\},$$

$$C_{44} = \frac{2}{\sqrt{3}c} \{3g_{1} + 9g_{3} + G_{1} + 4G_{2} + 14G_{3}\},$$

$$C_{13} = \frac{4}{\sqrt{3}a} \{\sqrt{3}D_{1} + \sqrt{3}D_{2} + 3E_{3} + 2\sqrt{3}D_{3}\} - C_{44},$$

(D.27)

where

$$P = \frac{4\{(A_1 - B_1) + (A_2 - B_2) + 2(A_3 - B_3) + 2\sqrt{3}F_3\}^2}{(A_1 + B_1) + (A_2 + B_2) + 2(A_3 + B_3)}$$

The constraint deduced from the condition of rotational invariance Equation (1.16) for the six neighbor MAS model is

$$\gamma^{2} \left[\frac{1}{3}^{a}_{2} + \frac{1}{8} \left[(A_{1} + B_{1}) + (A_{2} + B_{2}) + 2(A_{3} + B_{3}) \right] \right] = (D.28)$$

$$\frac{1}{2} g_{1} + \frac{3}{2} g_{3} + \frac{1}{6} G_{1} + \frac{2}{3} G_{2} + \frac{7}{3} G_{3} .$$

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This condition requires that the slopes of the TA[001] and TA₁[100] branches near q=0 are identical.

The equations of motion for an hcp crystal in the symmetry directions in terms of the interplanar force constants h_i and P_i (i=0,1,2,3) are given below (74) and the AFC composition of the interplanar force constants are given in Table 24.

$$\begin{bmatrix} 001 \end{bmatrix} (\Delta) \qquad m\omega^{2} = h_{1}\{1 - \cos(\pi cq)\} + h_{2}\{1 - \cos 2\pi cq\}$$
(reduced zone scheme) (D.29)
$$\begin{bmatrix} 100 \end{bmatrix} (\Sigma) \qquad m(\omega_{A}^{2} - \omega_{o}^{2}) = p_{o} + p_{1} \cos(\sqrt{3}\pi aq) + p_{2} \cos(\sqrt{3}2\pi aq)$$

$$\begin{bmatrix} 110 \end{bmatrix} (T) \qquad T0(T_{3})m\omega^{2} = h_{1}\{1 - \cos \pi aq\} + h_{2}\{1 - \cos 2\pi aq\}$$

$$T0(T_{2})m\omega^{2} = p_{o} + p_{1} \cos(\pi aq) + p_{2} \cos(2\pi aq) + p_{3} \cos(3\pi aq)$$

Using the MAS force constants the equations of motion written directly in terms of the atomic force constants are (42)

		 A1	A ₂	A ₃	a ₁	a ₂	a3	B ₁	B ₂	B ₃	b ₁	b ₂	b ₃	G1	G ₂	G ₃	g ₁	9 ₂	93
L[001]	h ₁													6	6	12			
Δ1Δ2	h ₂																	2	
T[001]	h1	3	3	6		1		3	3	6		1							
4546	h ₂					2						,							
L[100] _{Σ1}	P0 P1 P2	6	6	12			6 -6	6	6	12	8 -8		6 -1 -4						
τ ₁ [100] Σ ₃	P0 P1 P2													12	12	24	8 -8	-4	12 -8
τ ₁₁ [100] _{Σ4}	P0 P1 P2	6	6	12	8 -8		6 -2 -4	6	6	12			6 -6						
TA[110] T ₃	h ₁ h ₂ h ₃													4	4	4 4 4	4 2		4
то[110] Т ₂	P0 P1 P2 P3													8 4	8 4	12 4 4 4	6 -4 -2		4 -4
]			1			1					

Table 24. Force constant composition of interplanar force constants for an hcp crystal

[001] A

$$(\omega_{TA})^{2} = (\omega_{a}^{2}/2)(1-C_{1z}) + (2\beta_{4x}/m)(1-C_{2z}) ,$$

$$(\omega_{LA})^{2} = (\omega_{b}^{2}/2)(1-C_{1z}) + 2(\alpha_{4}+\beta_{4z})/m (1-C_{2z}) , \qquad (D.30)$$

$$(\omega_{T0})^{2} = (\frac{1}{2}\omega_{a}^{2})(1+C_{1z}) + (2\beta_{4x}/m)(1-C_{2z}) ,$$

$$(\omega_{L0})^{2} = (\frac{1}{2}\omega_{b}^{2})(1+C_{1z}) + (2(\alpha_{4}+\beta_{4z})/m)(1-C_{2z})$$

and at the zone boundary (A) $q = (0,0,\pi/c)$ and the frequencies are

$$(\omega_{T0})^{2}[q=(0,0,\pi/c)] = (\omega_{TA})^{2}[q=(00\pi/c)] = \omega_{a}^{2}/2 + 4\beta_{4x}/m ,$$

$$(\omega_{L0})^{2}[q=(0,0,\pi/c)] = (\omega_{LA})^{2}[q=(00\pi/c)] = \omega_{b}^{2}/2 + (4\alpha_{4}+4\beta_{4z})/m$$

,

where

$$\begin{split} \omega_{a}^{2} &= (12/m) \{ \varepsilon_{1x} + \varepsilon_{3x} + 2\varepsilon_{5x} + 2\delta_{1} + 8\delta_{3} + 28\delta_{5} \} , \\ \omega_{b}^{2} &= (12/m) \{ (\varepsilon_{1z} + \varepsilon_{3z} + 2\varepsilon_{5z}) + 3\gamma^{2} (\delta_{1} + \delta_{3} + 2\delta_{5}) \} , \\ C_{nz} &= \cos nq_{z}^{\frac{1}{2}}c, \ n=1,2,\ldots. \end{split}$$

[100] ₂

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At the zone boundary (M) q=($2\pi/\sqrt{3}a$,0,0) and the frequencies are given by

$$(\omega_{L0})^{2} = 1/m\{16\delta_{1} + 4\epsilon_{1x} + 96\delta_{3} + 12\epsilon_{3x} + 128\delta_{5} + 8\epsilon_{5x} + 6\alpha_{2} + 8\beta_{2x} + 2\alpha_{6} + 8\beta_{6x}\},$$

$$(\omega_{LA})^{2} = 1/m\{8\delta_{1} + 8\epsilon_{1x} + 208\delta_{5} + 16\epsilon_{5x} + 6\alpha_{2} + 8\beta_{2x} + 2\alpha_{6} + 8\beta_{6x},$$

$$(\omega_{T0})^{2} = 1/m\{24\delta_{1} + 8\epsilon_{1x} + 240\delta_{5} + 16\epsilon_{5x} + 2\alpha_{2} + 8\beta_{2x} + 6\alpha_{6} + 8\beta_{6x}\},$$

$$(D.31)$$

$$(\omega_{TA_{11}})^{2} = 1/m\{4\varepsilon_{1x} + 96\delta_{3} + 12\varepsilon_{3x} + 96\delta_{5} + 8\varepsilon_{5x} + 2\alpha_{2} + 8\beta_{2x} + 6\alpha_{6} + 8\beta_{6x}\},$$

$$(\omega_{TA_{\perp}})^{2} = 1/m\{12\gamma^{2}\delta_{1} + 36\gamma^{2}\delta_{3} + 24\gamma^{2}\delta_{5} + 4\varepsilon_{1z} + 12\varepsilon_{3z} + 8\varepsilon_{5z} + 8\beta_{2z} + 8\beta_{6z}\},$$

$$(\omega_{TO_{\perp}})^{2} = 1/m\{24\gamma^{2}\delta_{1} + 48\gamma^{2}\delta_{5} + 8\varepsilon_{1z} + 16\varepsilon_{5z} + 8\beta_{2z} + 8\beta_{6z}\},$$

[110] т

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At the zone boundary (K) $q=\frac{2}{3}\sqrt{2\pi}a(110)$ and the frequencies are given by

$$(\omega_{L0})^{2} = (\omega_{LA})^{2} = \frac{1}{2}\omega_{a}^{2} + \frac{9}{2}m[\alpha_{2}+2\beta_{2x}] ,$$

$$(\omega_{T0}_{11}) = \frac{1}{2}\omega_{a}^{2} + (1/m)[\frac{9}{2}\alpha_{2} + 9\beta_{2x} + 12\delta_{1} + 48\delta_{3} - 156\delta_{5}] ,$$

$$(\omega_{TA}_{11}) = \frac{1}{2}\omega_{a}^{2} + (1/m)[\frac{9}{2}\alpha_{2} + 9\beta_{2x} + 12\delta_{1} - 48\delta_{3} + 156\delta_{5}] ,$$

$$(\omega_{T0}_{L})^{2} = (\omega_{TA}_{L})^{2} = \frac{1}{2}\omega_{b}^{2} + 9\beta_{2z}/m .$$

(Notice that the degeneracies at the points A and K are consistent with those given in Appendix C, Equation (C.5b).)