CHAPTER-FOUR
CHAPTER - FOUR

DEVELOPMENT OF PRESENT MODEL

4.1 INTRODUCTION:

In the present chapter we have developed the necessary theory for studying lattice dynamics of hcp transition and rare earth metals. For transition metals we consider core-core interaction for electrons of d-shell. However in the case of rare earth metals core-core interaction is mediated by f shell f shell electrons.

4.2 MODEL FOR TRANSITION METALS:

In the case of transition metals the atoms in a solid are assumed to be composed of three entities (a) the conduction electrons which are spread through out the solid, (b) a shell of outer most d-electrons and (c) the ion core, which consists of the nucleus plus the remaining core electrons which are taken to move rigidly with the nucleus. From first principles within harmonic approximation the vibrational energy of the system of atoms can be described as

\[ V = V^{c-e} + V^{d-d} + V^{c-d} - \frac{\varepsilon}{\varepsilon} \left\{ V^{c-e} + V^{d-d} \right\} \]  

(4.1)

Where \( V^{c-e} \) is the second order change in the potential energy with respect to the displacement of ion core and due to interaction between ion cores.
V^{\text{d-d}}$ is the second order change in the potential energy between d-electron shells. $V^{\text{c-c}}$ and $V^{\text{d-e}}$ are the second order changes arising from the interaction between the conduction electrons and the ion core, and the shell of d-electron respectively. \( \varepsilon \) is the dielectric function arising from the interaction between the conduction electrons. Similarly $V^{\text{c-d}}$ is the change in the potential energy arising from the interaction between the ion core and its shell of d-electrons. Since ion cores are well localized the interaction between them can be taken in the coulomb-interactions between the point charges. The interaction between the conduction electrons and the ion core and d-electrons can be considered as the interaction of the conduction electrons with the respective potential arising from the ion core and d-electrons.

The potential energy terms in equation (4.1) are dependent on the product of the displacements of the ions cores and d-electron charge distribution. It may therefore be written as

\[
V = V^{\text{c-c}} \left\{ U(l, c) U(l', c') \right\} - V^{\text{c-c}} \left\{ U(l, c) U(l', c') \right\} \\
+ V^{\text{c-e}} \left\{ U(l, c) U(l', c') / \varepsilon \right\} + V^{\text{d-d}} \left\{ U(l, d) U(l', d') \right\} \\
- V^{\text{d-e}} \left\{ U(l, d) U(l', d') \right\} / \varepsilon \\
+ V^{\text{c-d}} \left\{ U(l, c) U(l, d) \right\} 
\] (4.2)

First three terms in (4.2) are analogous to the potential energy terms for simple metals. Let us replace these terms by $V_1$. The next three terms of equation (4.2) are due to shell of d-electrons. These may be replaced by $V_2$ thus
\[ V = V_1 \{ U(1,c)U(1',c') \} + V_2 \{ U(1,d)U(1',d') \} + V^{c-d} \{ U(1,c)U(1',d') \} \]  

(4.3)

\( U(1,c) \) and \( U(1',c') \) are the displacements of the cores designated by \( c \) and \( c' \) situated within 1th and 1' th unit cells. (Likewise) \( U(1,d) \) and \( U(1',d') \) are the similar term representing displacements for the corresponding cells. The potential energy \( V_1 \) obviously consists of (i) core–core and (ii) core and conduction electrons interaction. The former gives right to the short range forces where as the latter gives rise to the long range forces. Likewise \( V_2 \) may also be regarded to consist of similar terms.

Within the Born – open heimor [1] and harmonic approximation to ionic motion is determined by Schrodinger equation

\[ \{ T(R) + V(R) \phi(R) \} = E_{q} \phi(R) \]  

(4.4)

Where \( T \) is the Kinetic energy of cores and shells of d-electrons. The phonon frequencies \( \omega^2 (q) \) can be obtained as a solution of the secular determinant equation (1.33).

\[ \left| D(q) - \omega^2 I \right| = 0 \]  

(4.5)

Where \( I \) is the unit matrix \( D(q) \) is a (6x6) dynamical matrix defined by

\[ D(q) = R + S^{-1} K \]  

(4.6)
$R$ and $S$ both are again (6x6) dynamical matrices belonging to core –core and shell –shell interaction. $K$ describes the interaction between core and its shell of d-electrons in transition metals $S^{-1}$ is the inverse of $S$. Thus

$$R = \begin{pmatrix} R(\bar{q},cc)R(\bar{q},cc') \\ R'(\bar{q},cc')R(\bar{q},cc) \end{pmatrix}$$

$$S = \begin{pmatrix} S(\bar{q},dd)S(\bar{q},dd') \\ S'(\bar{q},dd')S(\bar{q},dd) \end{pmatrix}$$

and

$$K = K^2 \delta_{\alpha \beta}$$

$$\begin{bmatrix} \delta_{\alpha \beta} = 1 & \text{when } \alpha = \beta \\ \delta_{\alpha \beta} = 0 & \text{when } \alpha \neq \beta \end{bmatrix}$$

and zero when $\alpha \neq \beta$.

In view of the equation (4.3) the dynamical matrices corresponding to core and shell-shell interaction are given by

$$R_{\alpha \beta}(q,cc) = \frac{1}{M} \sum \frac{\partial^2 V_1}{\partial U_\alpha(1,c)\partial U_\beta(1',c')} \bigg|_0 \delta_{\bar{q},\bar{r}_i} e^{-i(\bar{q},\bar{r}_i)} (c \neq c')$$

$$R_{\alpha \beta}(q,cc) = \frac{1}{M} \left\{ \sum \frac{\partial^2 V_1}{\partial U_\alpha(1,c)\partial U_\beta(1',c')} \bigg|_0 e^{-i(\bar{q},\bar{r}_i)} \right\}_{c = c'}$$

$\tilde{R}_c$ is the equilibrium separation between $(1,c)$th and $(1',c')$th ions such that
\[ \vec{R}_c = \left( \vec{R}^o_{1c} - \vec{R}^o_{rc} \right) \]

Similarly

\[ S_{\alpha \beta}(q, dd') = \frac{1}{m} \left\{ \sum_{\alpha \beta} \frac{\partial^2 V_2}{\partial U_{\alpha}(l,d) \partial U_{\beta}(l',d')} \right\}_o e^{-i(q \cdot \vec{R}_c)} \quad |d \neq d' \quad (4.9) \]

\[ S_{\alpha \beta}(q, dd) = \frac{1}{m} \left\{ \sum_{\alpha \beta} \frac{\partial^2 V_2}{\partial U_{\alpha}(l,d) \partial U_{\beta}(l',d')} \right\}_o e^{-i(q \cdot \vec{R}_c)} \]

\[ R_{\alpha \beta}(q, cc) = \frac{1}{M} \left\{ \sum_{\alpha \beta} \frac{\partial^2 V_2}{\partial U_{\alpha}(l,d) \partial U_{\beta}(l,d)} \right\}_d e^{-i(q \cdot \vec{R}_c)} \quad |d = d' \quad (4.10) \]

Where \( \alpha, \beta = 1,2,3 \). \( M \) and \( m \) are masses of core and shell respectively. \( |_o \) denotes the derivatives of potential energies evaluated when lattice is in equilibrium.

4.3 MATRIX ELEMENTS CORRESPONDING TO CORE-CORE INTERACTION:

The potential energy \( V_1 \) in equation (4.3) obviously consist of (a) core-core and (b) core conduction electrons interactions. The former has the character of short range interaction whereas latter is described by long range interactions. Thus

\[ V_1 = V_{1s}^{e-r} + V_{1s}^{l-r} \]

In the pseudopotential approach the short range core-core interaction shall be expressed as the electrostatic Coulomb interaction between ion cores (c,c). The dynamical matrix for this part is \( D_{\alpha \beta}^{es} (q) \). The long range interaction gives the
band structure energy matrix element $D_{αβ}^{ss}(q)$. Thus the resultant matrix elements in equation (1.33) is

$$D_{αβ}(q,kk') = D_{αβ}^{ss}(q,kk') + D_{αβ}^{hs}(q,kk')$$

In view of equations (4.1) to (4.10) we shall be using $R_{αβ}(q,cc')$ in place of $R_{αβ}(q,kk')$ for matrix elements between ion cores and c', similarly symbol $S_{αβ}(q,dd')$ shall be used in place of $D_{αβ}(q,kk')$ for matrix elements between atom shells d and d'.

### 4.4 EVALUATION OF COULOMBIC MATRIX ELEMENTS $D_{αβ}^{es}(q)$ or $R_{αβ}^{es}(q)$

The Coulombic term $D_{αβ}^{es}(q)$ of the total dynamic matrix elements (4.11) can be evaluated by employing Ewald’s method for the lattice sum as derived from methods due to Thompson [2] and Kellermann [3]. Roy and Venkatraman [4] have given the detailed expression for $D_{αβ}^{es}(q)$. In the more proper from the Hermitian Coulombic contribution to dynamical matrix has been given by King [5] for non-cubic lattices in the harmonic approximation. According to Fuch [6], the Ewald’s electrostatic energy per ion is given by

$$E^{es} = \frac{Ze^2}{2} \lim_{q \to \infty} \left[ \frac{4\pi}{\Omega_o} \sum_{q} \frac{e^{-i(q^2/4\eta^2)}}{q^2} S^{*}(q)S(q) - \frac{2\eta}{\sqrt{\pi}} \right]
+ \sum_{j} G(\eta/\bar{r}_j) \frac{\pi}{(\Omega_o \eta^2)}$$

(4.12)
Where \( z^* \) is the effective valence of metal, \( \Omega_0 \) the atomic volume, \( S(\vec{q}) \) the usual structure factor and \( r_j \) the distance from a particular ion its \( j \)th neighbour. Function \( G(x) \) is defined by

\[
G(x) = \frac{2}{\sqrt{\pi}} \int e^{-x^2} \, dx
\]

(4.13)

\( \eta \) is a parameter to be chosen to optimize the convergence of two sums. For a fixed structure \( E^{es} \) can be written as

\[
E^{es} = \frac{Z^2 e^2}{r_0} \alpha
\]

(4.14)

\( \alpha \) is the geometric coefficient known as the madelung constant and the value 1.79168 for hexagonal close packed metals. The atomic radius \( r_s \) is related to its volume by the expression

\[
r_s = \left( \frac{3\Omega_0}{4\pi} \right)^{1/3}
\]

(4.15)

We wish to compute the change in electrostatic energy due to the introduction of distortion and therefore should subtract the electrostatic energy [7] of the undistorted crystal. We are left with

\[
\delta E^{es} = \frac{2\pi Z^2 e^2}{\Omega_0} \lim_{\eta \to \infty} \sum' \delta S^*(\vec{q}) \delta S(\vec{q}) \frac{e^{- (q^2 / 4\eta^2)}}{q^2}
\]

(4.16)

The calculations, using this dynamical matrix result in real eigenvalues, satisfying the Hermiticity, requirement, the relevant expression [8] are given as follows.
$$R_{\alpha\beta}^{es}(q_{cc}) = D_{\alpha\beta}^{es}(\tilde{q}, kk) = \frac{4\pi (Z^e)^2}{n\Omega_m} \sum_{\alpha} \left( \frac{\hat{h} + \tilde{q}}{\hat{h} + \tilde{q}} \right)_\alpha \left( \frac{\hat{h} + \tilde{q}}{\hat{h} + \tilde{q}} \right)_\beta \exp \left( \frac{-|\tilde{h} + \tilde{q}|^2}{4\eta^2} \right)$$

$$- \sum_{\beta} \left( \frac{\tilde{h}}{|\tilde{h}|} \right)_\beta \exp \left( \frac{-|\tilde{h}|^2}{4\eta^2} \right) \left\{ 1 + \cos (\tilde{h} \cdot \tilde{r}(kk')) \right\}$$

$$+ \frac{(Z^e)^2}{m} \sum_{\beta} \exp (i\tilde{q} \cdot \tilde{r}(1,k)) \left[ \frac{\text{erfc}(\eta) \tilde{r}(1,k)}{|\tilde{r}(1,k)|^3} \right]$$

$$+ 2\eta \exp (-\eta^2) |\tilde{r}(1,k)|^2 \delta_{\alpha\beta} - \frac{\tilde{r}(1,k)_{\alpha} \tilde{r}(1,k)_{\beta}}{|\tilde{r}(1,k)|^2} \right\}$$

$$\frac{3\text{erfc}(\eta/|\tilde{r}(1,k)|)}{|\tilde{r}(1,k)|^3} + \frac{6\eta \exp (-\eta^2) |\tilde{r}(1,k)|^2}{\sqrt{\pi} |\tilde{r}(1,k)|^2}$$

$$+ \frac{4\eta^3 \exp (-\eta^3 |\tilde{r}(1,k)|^2)}{\sqrt{\pi}} \right\}$$

$$\frac{(Z^e)^2}{m}$$

$$\left\{ \frac{\text{erfc}(\eta/|\tilde{r}(1,k)|)}{|\tilde{r}(1,k)|^3} \right\}$$

$$\frac{2\eta \exp (-\eta^2 |\tilde{r}(1,k')|^2)}{\sqrt{\pi} |\tilde{r}(1,k)|^2} \delta_{\alpha\beta}$$

$$\left\{ \tilde{r}(1,k'), \tilde{r}(1,k') \right\}_{\alpha} \left\{ \tilde{r}(1,k'), \tilde{r}(1,k') \right\}_{\beta}$$

$$\frac{3\text{erfc}(\eta) |\tilde{r}(kk')|}{|\tilde{r}(1,k')|^3}$$

$$\frac{6\eta \exp (-\eta^2 |\tilde{r}(1,k')|^2)}{\sqrt{\pi} |\tilde{r}(1,k')|^2} + \frac{4\eta^3 \exp (\eta^2 |\tilde{r}(1,k')|^2)}{\sqrt{\pi} |\tilde{r}(1,k')|^2} \right\}$$

(4.17)

For \( k = k' \)
\[ R_{\alpha\beta}^{eq}(q,cc') = D_{\alpha\beta}^{eq}(q, KK') = \frac{4\pi(z'c)^2}{m\Omega_0 n} \sum_{\lambda} (\bar{h} + \bar{q})_{\alpha} (\bar{h} + \bar{q})_{\beta} \exp \left( -\frac{(|\bar{h} + \bar{q}|^2}{4\eta^2} \right) \]

\[ \exp(-i(\bar{h} + \bar{q}) \cdot r(kk') + \frac{(z'c)^2}{m} \sum_{i} \left[ \frac{\text{erfc}(\eta|\bar{r}(1,kk'))}{|\bar{r}(1,kk')|^3} \right] \]

\[ + \frac{2n}{\sqrt{\pi}} \exp(-\eta^2|\bar{r}(1,kk')|^2) \delta_{\alpha\beta} \left\{ \frac{|\bar{r}(1,kk')|^2}{|\bar{r}(1,kk')|^2} \right\} + \frac{3\text{erfc}(\eta|\bar{r}(1,kk')|)}{\sqrt{\pi}} + \frac{6\eta}{\sqrt{\pi}} \exp(-\eta^2|\bar{r}(1,kk')|^2) \exp \{iq\bar{r}(1,kk') \} \]

(4.18)

In these expressions

\[ \bar{r}(1,kk') = \bar{r}(1,k) + \bar{r}(kk') \]

(4.19)

Where \( \bar{r}(kk') \) is the distance vector between the two atoms, \( \bar{h} \) a reciprocal lattice vector, and \( Z' \) the effective charge of the ion, which is different from the true valence \( Z \) because of the effects connected with the orthogonaliztion of the conduction electron wave function with core states. The complementary error function of argument \( x \) appearing in above expression is given by the relation.

\[ \text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^2} \, dt \]

(4.20)

Having given the details of the standard method involved in the evaluation of Coulombic part of the matrix elements; now we shall discuss the
band structure energy and its contribution to matrix elements for hcp structure. Expression for \( S_{\alpha\beta}^{\epsilon}(q,dd) \) and \( S_{\alpha\beta}^{\epsilon}(q,dd') \) are analoges to equations (4.17) and (4.18).

### 4.5 THE BRAND STRUCTURE MATRIX ELEMENTS \( D_{\alpha\beta}^{hs}(q) \) or \( R_{\alpha\beta}^{hs}(q) \)

In the second order perturbation theory the energy of the electron in the state \( \vec{K} \) is

\[
E(k) = \frac{\hbar^2 k^2}{2m} <\vec{K}|w|\vec{K}> + \sum_q \frac{<\vec{K}+q|w|\vec{K}> <\vec{K}|w|\vec{K}+\vec{q}>}{\hbar^2/2m \left(k^2 - \frac{\vec{q}^2}{2m}\right)}
\]

(4.21)

One is usually concerned with the last term for the study of thermal properties of the crystal interchanging the summation over \( \vec{q} \) with the integration over \( \vec{K} \) gets

\[
\sum_q s^*(\vec{q})s(\vec{q}) \frac{2\Omega_0}{(2\pi)^3} \int_{\vec{k}_F} d^3k <\vec{K}+\vec{q}|w|\vec{K}> <\vec{K}|w|\vec{K}+\vec{q}>
\]

(4.22)

It is interesting to note that the expression to the right of \( s^*(\vec{q})s(\vec{q}) \) is the function of wave number \( \vec{q} \) and is determined entirely by the local potential \( w(\vec{r}) \) and by the volume of the system. Furthermore, because of the spherical symmetry of \( w(\vec{r}) \) this is the function of the magnitude of \( \vec{q} \) only. The function is known is the “Energy Wave Number Characteristic” and is denoted by \( F(q) \). The expression for the band structure energy is, therefore, written as

\[
E^{hs} = \sum_q s^*(\vec{q})s(\vec{q}) F(q)
\]

(4.23)
Since the coulomb interaction between any two electrons is counted twice by this method [7], an energy equal to this interaction as given by the expression

\[
E_{\text{c-c}} = \frac{q^2 \Omega_0}{8\pi e^2} \sum_q |w'q|^2
\]  

(4.24)

must be subtracted from the expression for \( F(q) \). Thus [7]

\[
F(q) = \frac{2\Omega_0}{(2\pi)^3} \int_{k<\alpha} d^3k \left\langle \tilde{K} + \tilde{q} \right| w' \left| \tilde{K} \right\rangle \left\langle \tilde{K} \right| w' \left| \tilde{K} + \tilde{q} \right\rangle - \frac{q^2 \Omega_0}{8\pi e^2} |w'q|^2
\]  

(4.25)

The integral in the expression for \( F(q) \) may be solved to give

\[
F(q) = -\frac{\Omega_0 q^2}{8\pi e^2} \left\langle \tilde{K} + \tilde{q} \right| w' \left| \tilde{K} \right\rangle \left\langle \tilde{K} \right| w' \left| \tilde{K} + \tilde{q} \right\rangle \frac{\varepsilon'(q) - 1}{\varepsilon(q)}
\]  

(4.26)

\( \varepsilon(q) \) is Hartree dielectric function. It does not incorporate the effect of exchange and correlation between conduction electrons. In view of such effects the expression for \( F(q) \) gets modified in the following form

\[
F(q) = -\frac{\Omega_0 q^2}{8\pi e^2} \left\langle \tilde{K} + \tilde{q} \right| w' \left| \tilde{K} \right\rangle \left\langle \tilde{K} \right| w' \left| \tilde{K} + \tilde{q} \right\rangle \frac{\varepsilon'(q) - 1}{\varepsilon(q) \{1 - f(q)\}}
\]  

(4.27)

Where \( \varepsilon'(q) \) is the modified expression for the dielectric function involving exchange and correlation effects. Actual expression for \( \varepsilon'(q) \) is given in the chapter. Function \( f(q) \) takes into account of exchange and correlation interactions among conduction electrons. Various treatments to evaluate \( f(q) \) are given in brief in chapter VI.

Some authors [9] used a normalized \( F(q) \) defined as
\[
F_N(q) = - F(q) \left( \frac{2\pi z^2 e^2}{q^2 \Omega_0} \right)^{-1}
\]

Where the limit of \( F(q) \) as \( \bar{q} \to 0 \) is

\[
\hat{F}(q) \Rightarrow - \frac{2\pi z^2 e^2}{q^2 \Omega_0}
\]

Matrix elements corresponding to the band structure part is given by

\[
R_{\alpha\beta}^{bs} (q, cc) = D_{\alpha\beta}^{bs} (q, kk) = - \frac{4\pi z^2 e^2}{mn \Omega_0} \sum_{\vec{h}} \frac{(\vec{h} + \bar{q})_\alpha (\vec{h} + \bar{q})_\beta}{|\vec{h} + \bar{q}|} F_N(|\vec{h} + \bar{q}|) \{ 1 + \cos(\vec{h} \cdot \vec{r}(kk')) \}
\]

\[
R_{\alpha\beta}^{bs} (q, cc) = D_{\alpha\beta}^{bs} (q, kk) = - \frac{4\pi z^2 e^2}{mn \Omega_0} \sum_{\vec{h}} \frac{(\vec{h} + \bar{q})_\alpha (\vec{h} + \bar{q})_\beta}{|\vec{h}|^2} F_N(|\vec{h} + \bar{q}|) \exp[-i\vec{h} \cdot \vec{r}(kk')]
\]

Here \( \vec{h} \) is a reciprocal lattice vector, \( \bar{q} \) is the phonon wavevector, \( n \) is the number of ions per unit cell, \( m \) is the mass of the ions. \( \Omega_0 \) is the atomic mass. \( \vec{r}(kk') \) is the distance between \( k \) and \( k' \) type of atoms. Again in view of equations 4.1 to 4.10 we have used symbols \( R_{\alpha\beta}^{bs} (q, cc) \) and \( R_{\alpha\beta}^{bs} (q, cc') \) for matrix elements corresponding to the band structure interaction between ions cores. Similar expression between atomic shells (d,d’) can be written using above equations.
4.6 SELF-CONSISTENT DIELECTRIC SCREENING OF THE PSEUDOPOTENTIAL:

The screening plays as important role in the behaviour of metals that any understanding of metals which does not include a feeling for screening in a sense illusory. Furthermore, a description of self-consistent screening in terms of the pseudopotential is rather simple. Electrons not only interact with each ion through a local potential \( w^0(\vec{r}) \) but also interact with each other through a Coulomb potential \( w'(\vec{r}) \) which may be determined from the charge density due to all electrons i.e. a self-consistent field. Thus \( \vec{r} \) as given in equation (3.15) is

\[
\psi(\vec{r}) = w^0(\vec{r}) + w'(\vec{r})
\]

(4.30)

Using first order pseudowave functions we may compute the electron density or probability density and hence the field \( w'(\vec{r}) \). The value of \( \phi^*\phi \) to the first order is given by

\[
\phi^*\phi = \frac{1}{\Omega} \left[ 1 + \sum_q \{ C_q(\vec{K}) e^{iq\cdot\vec{r}} + C_q^*(\vec{K}) e^{-iq\cdot\vec{r}} \} \right]
\]

(4.31)

The sum of the above expression over the occupied electrons states within the Fermi sphere gives (besides from the constant term)

\[
n(\vec{r}) = \frac{2}{(2\pi)^3} \sum_q \int d^3k \{ C_q(\vec{K}) e^{iq\cdot\vec{r}} + C_q^*(\vec{K}) e^{-iq\cdot\vec{r}} \}
\]

(4.32)

Comparison of this expression with the Fourier component of \( n(\vec{r}) \) given by
\[ n(\vec{r}) = \sum_{q} n_q e^{i\vec{q}\cdot\vec{r}} \quad (4.33) \]

Gives
\[ n_q = \left[ \frac{2}{(2\pi)^3} \right] \int d^3k (C_q(\vec{k}) + C_q^*(\vec{k})) \quad (4.34) \]

Or
\[ n_q = -\frac{mk_e}{\pi^2 h^2} \frac{<\vec{k} + \vec{q}|w|\vec{k}>}{\frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right|} \quad (4.35) \]

Where \[ x = \frac{q}{2K_f} \]

The Poisson's equations \((\nabla^2 \phi = -4\pi \rho)\) is now used to obtain a relation between the screening potential \(W_q\) and electron density \(n_q\). This gives

\[ W_q = 4\pi e^2 n_q / q^2 \quad (4.36) \]

Eliminating \(n_q\) between (4.35) and (4.36), we write the results in the form

\[ <\vec{k} + \vec{q}|w|\vec{k}> = \frac{<\vec{k} + \vec{q}|w^0|\vec{k}>}{\varepsilon(q)} \quad (4.37) \]

With
\[ \varepsilon(q) = 1 + \frac{m^*e^2}{\pi k_f h^2 x^2} \left( \frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right| \right) \quad (4.38) \]

The screened potential may be obtained from the unscreened potential simply by division by a simple function of wave number \((\vec{q})\). This treatment is valid when \(w^0\) is a local potential. In view of equation (4.37) screened from factor may be written as

\[ <\vec{k} + \vec{q}|w|\vec{k}> = \frac{<\vec{k} + \vec{q}|w^0|\vec{k}>}{\varepsilon(q)} \quad (4.39) \]

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The function $\varepsilon (q)$ is called the static Hartree dielectric function for free electrons (refer to equation 3.22). It can readily be shown from (4.38) that the first derivative goes to minus infinity logarithmically at $2k_F$. Although the singularity is very small, it can have a large effect in properties depending upon the Fourier transform of the dielectric function. Lindhard [10] has also derived an expression for dielectric function using random phase approximation (RPA). According to him

$$\varepsilon_{\text{RPA}}(q) = 1 + Q_0(q)$$  \hspace{1cm} (4.40)

where $Q_0$, is the Lindhard electron polarizability times $-4\pi e^2 / q^2$, is

$$Q_0(q) = \frac{k^2 TF}{q^2} \left( \frac{1}{2} f(x) \right) + \frac{q}{2k_F}$$  \hspace{1cm} (4.41)

With

$$f(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|$$

And the Thomas Fermi Screening constant

$$K_{TF}^2 = \left( \frac{m^*}{m} \right) \left( \frac{4K_F}{\pi a_0} \right)$$  \hspace{1cm} (4.42)

Here $a_0$ is Bohr's radius, and $m^*$ is an effective electron mass introduced, following Price et al [11], to include band structure effects. Effects of the lattice on the conduction electrons are thus included in this average sense. It is noticeable that equations (4.38) and (4.40) are the same. The validity of Lindhard
expression is limited to high density electron region \((r_s \leq 1)\). Also this theory does not take into account for the short range effects.

4.7 EXCHANGE AND CORRELATION AMONG CONDUCTION ELECTRONS

Exchange among the conduction electrons can be included in first principle pseudopotential theory by assuming that the Fourier component of the total screening potential seen by an electron is

\[
W_q = \left( \frac{4 \pi e^2}{q^2} \right) + X_q \n_q
\]

\((4.43)\)

\(n_q\) is the conduction electron density, \(\frac{4 \pi e^2}{q^2}\) the transform of the Coulombic potential, and \(X_q\) is the exchange interactions. If \(W_q\) is expressed in terms of an unscreened element and some dielectric function we obtained, after some algebra,

\[
\varepsilon^*(q) = 1 + \left[ q^2 x_q \left/ (4 \pi e^2) \right. \right] \{ \varepsilon(q) - 1 \}
\]

\((4.44)\)

This equation is usually written as

\[
\varepsilon^*(q) = 1 + \left[ 1 - f(q) \right] \{ \varepsilon(q) - 1 \}
\]

\((4.45)\)

Function \(f(q)\) takes into account the exchange and correlation effects among the conduction electrons.
In recent years, various forms have been proposed for $f(q)$. Hubbard [12] in a classic paper, using diagram technique, made an attempt to include the effect of exchange between electrons of parallel spin. According to Hubbard [12]

$$f_H(q) = \frac{q^2}{2(q^2 + K_F^2)}$$ \hspace{1cm} (4.46)

Several other expression [13] for $f(q)$ have been given in chapter VI. We have used $f(q)$ expression of Singwi et al [14] in our work.

Singwi et al [14] developed self-consistent theory of the dielectric function of the electron liquid in the metallic density range, which takes into account the short range correlations arising from both Coulomb and exchange effect through a local field correlation depending upon the pair correlation function. In a more refined theory these authors considered the adjustment of the pair correlation function to the external weak field. In contrast to the earlier theory present theory satisfies closely the compressibility sum rule and also gives reasonable values for the pair correlation function. Singwi et al [14] have tabulated $f(q)$ values for different values of $q$. It is observed that these values can be fitted quite accurately with a function of the form

$$f_{SSL} (q) = A \left(1 - e^{-4\eta q^2}\right), \text{where } \eta = \frac{q}{2k_F}$$ \hspace{1cm} (4.47)

Values of parameter $A$ and $B$ have been reported by Singwi et al [14] for different values of $r_s$ in the range of metallic densities. Geldart and Taylor [15] made some comments on the theory of Singwi et al [14]. They concluded that
the number conservation was violated in this theory. This analysis of Geldart and Taylor was, however proved to be erroneous.

Vashista and Singwi [16] presented a modification of the theory of Singwi et al. [14], which has the merit of satisfying almost exactly the compressibility sum rule and of giving a satisfactory pair correlation function. In brief, this modification consists in allowing for the change in the pair correlation function $g^e(r)$. This then results in an additional term involving the density derivatives of $g^e(r)$ in the local field correlation of Singwi et al. [14]. In this case

$$f_{VS}(q) = \left[ 1 + an \frac{\partial}{\partial n} \right] \left[ -\frac{1}{n} \int \frac{dq'}{(2\pi)^3} \frac{q'\cdot q}{q'^2} S(q-q') - 1 \right]$$

The term in the large parenthesis is designated as $f(q)$ by Singwi et al [14]. In their first paper. Here 'a' in the expression for $f_{VS}(q)$ is treated as a parameter. Although VS have been unable to estimate the value of the parameter 'a' from first principles, yet it has been adjusted very carefully so that it suffices in the entire metallic density range. Function $S(q)$ in equation (4.48) is usual structure factor and $n$ is the electron density.

Recently, Pathak and Vashista [17] presented a theory of electron correlations based on a generalized random phase approximation. An expression for local field correlation is obtained using a third frequency moment of spectral function of the electron density response function. In this case function $f(q)$ is given by
For the sake of comparison we have plotted \( f(q) \) values for different theories as a function of \( q \) for \( r = 4 \) and \( 6 \) in Fig. 4.1 and 4.2 respectively. \( q \) is in units \( k_F \). It might be mentioned here that \( f(q) \) in the theories of Hubbard [12], and Toigo and Woodruff [18] is independent of \( r \). The \( q \to \infty \) limits of \( f(q) \) is marked by the broken lines at the right hand side of the Figs.

From the brief review on dielectric function as mentioned above it may be concluded that the self-consistent \( f(q) \) function as obtained by Vashista and Singwi [16] is the most suitable function because its satisfies almost exactly the compressibility sum rule [16] and physically acceptable pair correlation functions[16]. We have therefore chosen this \( f(q) \) function for our studies. Parameters appearing in the dielectric functions which have been used in the present studies are given in Table 4.1.

4.8 A TWO PARAMETER LOCAL MODEL POTENTIAL:

Most of the model pseudopotential a mentioned previously are described in \( \vec{r} \) space by a discontinuous function. Consequently, their Fourier transforms oscillate at large value of \( \vec{q} \) and do not ensure sufficiently rapid convergence of the series. When summing over reciprocal space, it is therefore, necessary to introduce artificially a rather arbitrary exponential damping factor.
Figure 4.1  $f(q)$ values are plotted for different theories as a function of $q$ for $r_5 = 4$. 
Figure 4.2  $f(q)$ values are plotted for different theories as a function of $q$ for $r_5 = 6$. 
**TABLE 4.1**

*Parameters appearing in the dielectric functions $\varepsilon^* (q)$*

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Metal</th>
<th>Parameters of $\varepsilon_{YS}^*(q)$</th>
<th>Parameters of $\varepsilon_{SSI}^*(q)$</th>
<th>Parameters of $\varepsilon_{GV}^*(q)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>1.</td>
<td>Zr</td>
<td>0.8419</td>
<td>0.3346</td>
<td>0.8883</td>
</tr>
<tr>
<td>2.</td>
<td>Y</td>
<td>0.8910</td>
<td>0.3226</td>
<td>0.9204</td>
</tr>
<tr>
<td>3.</td>
<td>Hf</td>
<td>0.9001</td>
<td>0.3212</td>
<td>0.9220</td>
</tr>
<tr>
<td>4.</td>
<td>Sc</td>
<td>0.9280</td>
<td>0.3140</td>
<td>0.388</td>
</tr>
<tr>
<td>5.</td>
<td>Ti</td>
<td>0.8920</td>
<td>0.3231</td>
<td>0.9185</td>
</tr>
<tr>
<td>6.</td>
<td>Ho</td>
<td>0.8812</td>
<td>0.3312</td>
<td>0.9086</td>
</tr>
<tr>
<td>7.</td>
<td>Tb</td>
<td>0.8961</td>
<td>0.3241</td>
<td>0.9172</td>
</tr>
</tbody>
</table>
Later, the above shortcoming has been removed by Krasko and Gursko [19] and also by Kushwaha and Rajput [20].

A simple bare ion local model pseudopotential which is free from the common shortcoming inherent with the previous model pseudopotential is given by

$$W^0(\vec{r}) = -\frac{z^2 e^2}{\epsilon r} + \left( \frac{z^2 e^2}{\epsilon r} + \beta \right) e^{-\alpha r}$$  (4.50)

Where $\alpha$ and $\beta$ are the model parameters. The convergence problem in the calculation of matrix elements $D_{\alpha\beta}^{0s}(\vec{q})$ due to oscillations of Fourier transform of 0.6384 so that the third term of equation (4.53) closely agrees with the detailed calculations of $\varepsilon_{ab}(\vec{p})$.

The bare ion potential as used in the present case is given by equation (4.50).

4.9 MODEL POTENTIAL FOR RARE EARTH METALS:

In this case 'f' electronic shell is incompletely filled and we can replace $V^{d-d}$ and $V^{d-c}$ expression by $V^{f-f}$ and $V^{f-e}$ in equation (4.1). Consequently the $S$ matrix equations (3.6) is redefined through the relation

Matrix elements of $s$ matrix are given by

$$D(q) = R + S^{-1} k$$  (4.54)

Where

$$R = \begin{pmatrix} R(q,cc) & R(q,cc') \\ R^*(q,cc') & R(q,cc) \end{pmatrix}$$

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And
\[ S = \begin{pmatrix} S(q, ff') & S(q, ff) \\ S'(q, ff') & S(q, ff) \end{pmatrix} \]

Matrix elements of \( S \) matrix are given by

\[ S_{\alpha\beta}(q, ff') = \frac{1}{m} \left[ \sum_i \left( \frac{\partial^2 V_2}{\partial u_{\alpha}(l, f) \partial u_{\beta}(l', f')} \right) \exp(-i\mathbf{q} \cdot \mathbf{R}_f) \right]_{R_f = R_i} \tag{4.55} \]

\[ S_{\alpha\beta}(q, ff') = \frac{1}{m} \left[ \sum_i \left( \frac{\partial^2 V_2}{\partial u_{\alpha}(l, f) \partial u_{\beta}(l', f')} \right) \exp(-i\mathbf{q} \cdot \mathbf{R}_f) \right]_{R_f = R_i} \tag{4.56} \]

Where \( \alpha, \beta = 1, 2, 3 \) denotes that the derivatives of potential energies have been defined for the lattice in equilibrium \( V_2 \) the potential energy given in equation (4.3) corresponds to incomplete \( f \) and \( f' \) shells. Expression for the dielectric constant (4.52) modifies to

\[ \varepsilon(\mathbf{p}) = 1 - \varepsilon_{ss}(\mathbf{p}) - \varepsilon_{fs}(\mathbf{p}) \]

Where \( \varepsilon_{fs} \) represents contribution from \( 'f' \) to \( 's' \) transition.

**4.10 EVALUATION OF MODEL PSEUDOPOTENTIAL PARAMETERS:**

The model pseudopotential parameters \( \alpha \) and \( \beta \) are evaluated by filling the experimental quantities on the right hand side of the following equations

\[ \frac{E}{N} = -E_b - E_i \tag{4.57} \]

\[ \Omega_0 \left[ \frac{\partial(E/N)}{\partial \Omega_0} \right]_0 = -\Omega_0 p = 0 \tag{4.58} \]
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Metal</th>
<th>$E_b$ (KeV)</th>
<th>$E_i$ (KeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Zr</td>
<td>8.659</td>
<td>0.001</td>
</tr>
<tr>
<td>2.</td>
<td>Y</td>
<td>17.038</td>
<td>0.025</td>
</tr>
<tr>
<td>3.</td>
<td>Hf</td>
<td>4.491</td>
<td>0.031</td>
</tr>
<tr>
<td>4.</td>
<td>Sc</td>
<td>4.491</td>
<td>0.032</td>
</tr>
<tr>
<td>5.</td>
<td>Ti</td>
<td>4.966</td>
<td>0.035</td>
</tr>
<tr>
<td>6.</td>
<td>Ho</td>
<td>55.618</td>
<td>0.023</td>
</tr>
<tr>
<td>7.</td>
<td>Tb</td>
<td>51.996</td>
<td>0.021</td>
</tr>
</tbody>
</table>
### TABLE – 4.3

Values of Physical Constants

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\nu(\Gamma_3^+)$ THz</th>
<th>m a.m.u.</th>
<th>Lattice constants</th>
<th>$\Omega_0$ (Å$^3$)</th>
<th>$K_F$ (Å$^{-1}$)</th>
<th>$Z^*$ (Å$^{-1}$)</th>
<th>$\eta$ (Å$^{-1}$)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>2.50</td>
<td>91.220</td>
<td>3.2331 5.1491</td>
<td>28.29</td>
<td>1.2070</td>
<td>2.1726</td>
<td>0.767</td>
<td>-2.430</td>
</tr>
<tr>
<td>Y</td>
<td>4.64</td>
<td>88.906</td>
<td>3.6470 5.7300</td>
<td>32.31</td>
<td>1.1009</td>
<td>2.0218</td>
<td>0.562</td>
<td>-0.188</td>
</tr>
<tr>
<td>Hf</td>
<td>3.10</td>
<td>170.490</td>
<td>3.1946 5.5050</td>
<td>11.13</td>
<td>1.7230</td>
<td>2.0952</td>
<td>0.612</td>
<td>-0.446</td>
</tr>
<tr>
<td>Sc</td>
<td>6.91</td>
<td>44.956</td>
<td>3.3090 5.2680</td>
<td>16.74</td>
<td>1.5259</td>
<td>2.0318</td>
<td>0.656</td>
<td>-0.139</td>
</tr>
<tr>
<td>Ti</td>
<td>4.17</td>
<td>47.900</td>
<td>2.5906 4.6788</td>
<td>8.95</td>
<td>1.8791</td>
<td>2.0263</td>
<td>0.570</td>
<td>-3.110</td>
</tr>
<tr>
<td>Ho</td>
<td>3.40</td>
<td>64.930</td>
<td>3.5713 5.6158</td>
<td>20.59</td>
<td>1.4130</td>
<td>2.1382</td>
<td>0.582</td>
<td>-0.330</td>
</tr>
<tr>
<td>Tb</td>
<td>3.25</td>
<td>158.925</td>
<td>3.5900 5.6900</td>
<td>21.01</td>
<td>1.4057</td>
<td>2.0631</td>
<td>0.506</td>
<td>-0.133</td>
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<tr>
<td>S. No.</td>
<td>Metal</td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>1.</td>
<td>Zr</td>
<td>4.2</td>
<td>25.6</td>
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</tr>
<tr>
<td>2.</td>
<td>Y</td>
<td>2.8</td>
<td>16.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Hf</td>
<td>4.7</td>
<td>27.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Sc</td>
<td>4.3</td>
<td>26.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Ti</td>
<td>5.2</td>
<td>31.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Ho</td>
<td>4.9</td>
<td>29.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Tb</td>
<td>4.4</td>
<td>26.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Where $E_b$ is binding energy per atom, $E_i$ is the ionization energy of each ion and $\Omega_0$ is the atomic volume. Knowing the experimental values of these energies, we find the values of the parameters. The experimental values for $E_b$ and $E_i$ for different h.c.p. metals are given in table 4.2.

Electrostatic energy was obtained in article 4.3. The band structure energy part, however, embodies two important ingredients like pseudopotential and dielectric screening function. In preceding sections we developed pseudopotential formulation and introduced the concept of dielectric screening and local filed correction. Now we shall use them to obtain matrix elements corresponding to the band structure part of the Energy.

Values of physical constants for transition and rare earth metals Zr, Y, Hf, Sc, Ti, Ho, and Tb have been given in Table 4.4. Value of the constant $K$ defining equation (4.6) has been determined using experimentally known frequency at the point $\Gamma'_1$. This frequency $\nu_{\Gamma_0 \Gamma'_1}$ is listed in Table 4.4.

The radii of summation in the direct lattice space and in reciprocal lattice space were chosen to be 3.0a (A) and $(\frac{2\pi}{a}) A^{0.1}$ respectively.

Values of model parameters $\alpha$, $\beta$ for different metals are given in Table 4.4.

4.11 PHONON DISPERSION RELATIONS FOR TRANSITION METALS:
The following expression for phonon dispersion relations along symmetry direction have been obtained. Readers are requested to refer to equation (4.1) to (4.10).

(a) [0001] direction

\[
\begin{align*}
M\omega^2_{\text{LO}} &= \frac{[R_{33}(\vec{q}, cc) + R_{33}(\vec{q}, cc')]}{[S_{33}(\vec{q}, dd) + S_{33}(\vec{q}, dd')]}
\end{align*}
\]

\[
\begin{align*}
M\omega^2_{\text{LA}} &= \frac{[R_{43}(\vec{q}, cc) - R_{33}(\vec{q}, cc')]}{[S_{33}(\vec{q}, dd) - S_{33}(\vec{q}, dd')]}
\end{align*}
\]

\[
\begin{align*}
M\omega^2_{\text{TO}} &= \frac{[R_{11}(\vec{q}, cc) + R_{11}(\vec{q}, cc')]}{[S_{11}(\vec{q}, dd) + S_{11}(\vec{q}, dd')]}
\end{align*}
\]

\[
\begin{align*}
M\omega^2_{\text{TA}} &= \frac{[R_{11}(\vec{q}, cc) - R_{11}(\vec{q}, cc')]}{[S_{11}(\vec{q}, dd) - S_{11}(\vec{q}, dd')]}
\end{align*}
\]

In this case \( \xi = \frac{q}{q_{\text{max}}} \) where \( q_{\text{max}} = \frac{\xi c}{c} \) and \( q_x = 0, q_y = 0, q_z = \frac{\xi \eta \pi}{c} \)

where \( 0 \leq \xi \leq 1 \).

(b) [01\overline{1}0] direction

\[
\begin{align*}
M\omega^2_{\text{LO}} &= \frac{[R_{11}(\vec{q}, cc) + R_{11}(\vec{q}, cc')]}{[S_{11}(\vec{q}, dd) + S_{11}(\vec{q}, dd')]}
\end{align*}
\]

\[
\begin{align*}
M\omega^2_{\text{TO}} &= \frac{[R_{11}(\vec{q}, cc) - R_{11}(\vec{q}, cc')]}{[S_{11}(\vec{q}, dd) - S_{11}(\vec{q}, dd')]}
\end{align*}
\]

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\[ Mw_{TO}^2 = \frac{[R_{33}(\vec{q},cc) + R_{33}(\vec{q},cc')]\vec{k}^2}{[S_{33}(\vec{q},dd) + S_{33}(\vec{q},dd')]\vec{k}^2} \]

\[ Mw_{TA}^2 = \frac{[R_{33}(\vec{q},cc) - R_{33}(\vec{q},cc')]\vec{k}^2}{[S_{33}(\vec{q},dd) - S_{33}(\vec{q},dd')]\vec{k}^2} \]

\[ Mw_{LO}^2 = \frac{[R_{22}(\vec{q},cc) + R_{33}(\vec{q},cc')]\vec{k}^2}{[S_{22}(\vec{q},dd) + S_{22}(\vec{q},dd')]\vec{k}^2} \]

\[ Mw_{LA}^2 = \frac{[R_{22}(\vec{q},cc) - R_{33}(\vec{q},cc')]\vec{k}^2}{[S_{22}(\vec{q},dd) - S_{22}(\vec{q},dd')]\vec{k}^2} \]

In this direction \( \xi = \frac{q}{q_{\text{max}}} \) where \( \xi = \frac{2\pi}{a\sqrt{3}} \) and \( q_x = 0, q_y = \frac{2\eta\pi}{a\sqrt{3}}, q_z = 0 \) \( (0 \leq \xi \leq 1) \).

(c) [1120] direction

\[ 2M \omega_{LO}^2 = [A_1 + B_1 + X_i]^{C-C} \frac{\vec{k}^2}{[A_1 + B_1 + X_i]^{d-d}} \]

\[ 2M \omega_{LA}^2 = [A_1 + B_1 - X_i]^{C-C} \frac{\vec{k}^2}{[A_1 + B_1 - X_i]^{d-d}} \]

\[ 2M \omega_{TO}^2 = [A_2 + B_2 + X_j]^{C-C} \frac{\vec{k}^2}{[A_2 + B_2 + X_j]^{d-d}} \]

\[ 2M \omega_{TA}^2 = [A_2 + B_2 - X_j]^{C-C} \frac{\vec{k}^2}{[A_2 + B_2 - X_j]^{d-d}} \]

\[ Mw_{TO}^2 = \frac{[R_{33}(\vec{q},cc) + R_{33}(\vec{q},cc')]\vec{k}^2}{[S_{33}(\vec{q},dd) + S_{33}(\vec{q},dd')]\vec{k}^2} \]

\[ Mw_{TA}^2 = \frac{[R_{33}(\vec{q},cc) - R_{33}(\vec{q},cc')]\vec{k}^2}{[S_{33}(\vec{q},dd) - S_{33}(\vec{q},dd')]\vec{k}^2} \]
Where

\[ A_1 = \left| R_{11}(\bar{q}, cc) \right| + \left| R_{11}(\bar{q}, cc') \right| \]
\[ B_1 = \left| R_{22}(\bar{q}, cc) \right| - \left| R_{22}(\bar{q}, cc') \right| \]
\[ X_1 = \left( (A_1 - B_1)^2 + 4c_1^2 \right)^{1/2} \]
\[ c_1 = I_m R_{12}(q, cc) - I_m R_{12}(q, cc') \]

Similarly

\[ A_2 = \left| R_{11}(\bar{q}, cc) \right| - \left| R_{11}(\bar{q}, cc') \right| \]
\[ B_2 = \left| R_{22}(\bar{q}, cc) \right| + \left| R_{22}(\bar{q}, cc') \right| \]
\[ X_2 = \left( (A_2 - B_2)^2 + 4c_2^2 \right)^{1/2} \]
\[ c_2 = I_m R_{12}(q, cc) + I_m R_{12}(q, cc') \]

Here A’s, B’s, and X’s have been defined for core - core (c-c) interaction. Similarly type of relations can be obtained for shell - shell (d-d) interaction.

In this direction the reduced wave vectors \( \xi = \frac{q}{q_{\text{max}}} \)

Where \( q_{\text{max}} = \frac{4\pi}{3a} \) and \( q_x = \frac{2\pi\eta}{3a} \) \( q_y = 0 \) \( q_z = 0 \) (0 \( \leq \eta \leq 1 \)).

In the expression for phonon dispersion relations along [001], [0110] and [1120] directions. M represents the ionic mass, suffixes L and T corresponds to longitudinal and transverse modes while 0 and A stand for optical and acoustic modes respectively c-c and d-d are symbols for core-core and shell - shell interaction.

These expression for dispersion relations of transition metals involve matrix elements \( S_{\alpha\beta}(q, dd') \) corresponding to d shell d’ shell interaction. Similar
expressions are used for rare earth metals in which f shell-f'shell interaction is involved.

4.12 THERMAL PROPERTIES:

A solid is capable of vibrating in different modes. The contribution of vibrational modes to the thermodynamic properties depends solely upon distribution function $G(u)$. For a finite lattice the frequency distribution function $G(u)$ is such that $G(u) \, dv$ represents the number of vibrational modes of the lattice in the frequency range $u$ and $(u + du)$. The direct experimental determination of frequency distribution function has been made possible only in few cases owing to various experimental difficulties. The most straightforward and direct method for determining $G(u)$ lies in determining the vibrational frequencies for a large number points within the first Brillouin zone. For this purpose in the present work the first Brillouin zone of hcp lattice has been divided into 1000 miniature cells. From the symmetry requirements of the lattice, these 1000 points are reduced to 84 non equivalent points including the origin lying within $1/24$th part of the first Brillouin zone which is irreducible under symmetry operations that leave the roots of the secular determinant unchanged. The vibrational frequencies are determined from the roots of the secular determinant for values of wave vectors corresponding to these non equivalent points. Each frequency is assigned a statistical weight according to number of similar points associated with it. When properly weighted, the vibration spectra corresponding to
these non equivalent points will represent the complete vibration spectra for the solid and the frequency destitution function can be obtained by making use of Blackman's [22] sampling technique. For sampling purpose, the entire frequency range is divided into number of small intervals of width $\Delta \nu = 0.2 \times 10^{12}$ Hz and all the frequencies falling into these intervals are counted with their proper statistical weights and from these the histogram representing the frequency distribution $G(\nu)$ is obtained.

The lattice specific heat at constant volume at temperature $T$ is given as.

\[
C_v = 3N_A K_B \frac{\int_0^{\nu_m} \left( \frac{\hbar \nu}{K_B T} \right)^2 \left[ \exp \left( \frac{\hbar \nu}{K_B T} \right) \right] G(\nu) \, d\nu}{\int_0^{\nu_m} G(\nu) \, d\nu}
\]

Where $\nu_m$ is the maximum frequency, $K_B$ Boltzmann constant, $\hbar$ the Plank's constant and $N_A$ th Avogadro number. When converted into summation convention to be used for computation the equation (6.1) becomes

\[
C_v = 3N_A K_B \frac{\sum E \left( \frac{\hbar \nu}{K_B T} \right) G(\nu) \Delta \nu}{\sum G(\nu) \Delta \nu}
\]

where $E \left( \frac{\hbar \nu}{K_B T} \right)$ is the Einstein function defined as with

\[
E(X) = \frac{X^2 \exp(X)}{[\exp(X) - 1]^2}
\]

With $X = \frac{\hbar \nu}{K_B T}$
$$R \text{ is gas constant}$$

$$G(v)\Delta v = \text{Total number of frequencies considered}$$

$$= 6000 \text{ (for hcp structure)}$$

So equation (6.2) can be written as

$$C_v = \frac{3N_A k_B}{6000} \sum v E(X) G(v) \Delta v$$

(4.62)

For calculation of specific heat the Einstein function corresponding to mid point of each interval $\Delta v = 0.2 \times 10^{12} \text{ Hz (say)}$ multiplied by its statistical weight gives the contribution of each interval to the specific heat. The statistical weight of the interval obtained from the number of frequencies lying in that interval. The contribution of all such interval when summed up give $E(X) G(v) \Delta v$. By using the expression (6.4) the lattice specific heat $C_v$ is then calculated.

At low temperature the mesh of points becomes too coarse to give accurate values for $C_v$ because of dominant effect of low frequency end of the spectrum. At very low temperature the contribution of the outer portions of the Brillouin zone to the specific heat gradually decreases and its value becomes increasingly dependant on the central part of Brillouin zone. The sampling technique is more useful only if the number of frequency falling in each frequency interval is fairly large.

In the present work, we have reported lattice specific heat for different hcp transition metals in the moderate temperature range 10-500 K. The calculated values of $C_v$ at different temperatures are compared with the
corresponding experimental values. The electronic specific heat contribution $\gamma_e T$ is subtracted from the measured specific heat at different temperatures.

The computed values of $C_V$ at different temperatures have been used for obtaining Debye characteristic temperature $\theta$ of these temperatures. The value of $\theta / T$ can be determined from $C_V - \theta / T$ table for any value of $C_V$ and hence $\theta$ for different temperature are calculated theoretically. These values of $\theta$ have been plotted against temperature and compared with experimental values which ever available.
REFERENCES