CHAPTER V

PHONON DISPERSION RELATIONS OF
HEXAGONAL CLOSE PACKED METALS

5.1 Introduction

In the lattice dynamical theory of hcp metals, it becomes quite necessary to have a detailed information as to how phonon waves behave along different symmetry directions in the lattice and how the vibrational modes are distributed throughout the whole frequency range of atomic oscillations. In this chapter we have used phenomenological model discussed in the preceding chapter for the study of phonon dispersion relations between frequency and wavevector along the symmetry direction of hcp metals.

5.2 Dispersion Relations Along Symmetry Directions

The dynamical matrix $\mathcal{D}(q)$ (equation 4.5) for hcp structure is of the order of $6 \times 6$. The solution of the secular equation for particular value of $q$ in three symmetry directions $[0001]$, $[0\bar{1}\bar{1}0]$ and $[\bar{1}1\bar{2}0]$ gives us six frequencies for six branches of dispersion relation out of which three will be acoustic and three optical. In two symmetry directions $[0001]$ and $[0\bar{1}\bar{1}0]$ the dynamical matrix $\mathcal{D}(q)$ diagonalises into three $(2 \times 2)$ matrices one describing the longitudinal and other two transverse vibrations. The two matrices for the transverse vibrations in $[0001]$ directions are degenerate but these are different in $[0\bar{1}\bar{1}0]$ directions.
The two transverse modes in [01\overline{1}0] are differentiated by labelling \( T_\| \) and \( T_\perp \) depending on their polarisation parallel and perpendicular to the basal plane.

In the third symmetry direction [1\overline{1}20], the secular determinant again reduces into \((4 \times 4)\) and \((2 \times 2)\) submatrices. The first submatrix of \((4 \times 4)\) is a complex matrix giving four frequencies parallel to basal plane while the second submatrix gives phonon frequencies corresponding to transverse vibrations with polarisation perpendicular to the basal plane.

Thus the following expressions for phonon dispersion relations along symmetry directions have been obtained.

(a) \([0001]\) direction

\[
\begin{align*}
M_{\omega^2}^{LO} &= \left[ R_{33}(\bar{q}, \bar{c}c) + |R_{33}(\bar{q}, \bar{c}'c')| \right] \\
&\quad - \frac{k^2}{\left[ S_{33}(\bar{q}, \bar{c}c) + |S_{33}(\bar{q}, \bar{c}'c')| \right]} \\
M_{\omega^2}^{LA} &= \left[ R_{33}(\bar{q}, \bar{c}c) - |R_{33}(\bar{q}, \bar{c}'c')| \right] \\
&\quad - \frac{k^2}{\left[ S_{33}(\bar{q}, \bar{c}c) - |S_{33}(\bar{q}, \bar{c}'c')| \right]} \\
M_{\omega^2}^{TO} &= \left[ R_{11}(\bar{q}, \bar{c}c) + |R_{11}(\bar{q}, \bar{c}'c')| \right] \\
&\quad - \frac{k^2}{\left[ S_{11}(\bar{q}, \bar{c}c) + |S_{11}(\bar{q}, \bar{c}'c')| \right]} \\
M_{\omega^2}^{TA} &= \left[ R_{11}(\bar{q}, \bar{c}c) - |R_{11}(\bar{q}, \bar{c}'c')| \right] \\
&\quad - \frac{k^2}{\left[ S_{11}(\bar{q}, \bar{c}c) - |S_{11}(\bar{q}, \bar{c}'c')| \right]}
\end{align*}
\]
In this case \( \tau = \frac{q}{q_{\text{max}}} \) where \( q_{\text{max}} = \frac{\pi}{c} \) and \( q_x = 0, q_y = 0, q_z = \frac{\eta n}{c} \) where \( 0 \leq \eta \leq 1 \).

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

\[
\begin{align*}
M_{\text{TOL}}^2 &= \left[ R_{11}(\vec{q}, \cc) + \left| R_{11}(\vec{q}, \cc') \right| \right] - \frac{\kappa^2}{\left[ S_{11}(\vec{q}, \dd) + \left| S_{11}(\vec{q}, \dd') \right| \right]} \\
M_{\text{TAL}}^2 &= \left[ R_{11}(\vec{q}, \cc) - \left| R_{11}(\vec{q}, \cc') \right| \right] - \frac{\kappa^2}{\left[ S_{11}(\vec{q}, \dd) - \left| S_{11}(\vec{q}, \dd') \right| \right]} \\
M_{\text{TO\perp}}^2 &= \left[ R_{33}(\vec{q}, \cc) + \left| R_{33}(\vec{q}, \cc') \right| \right] - \frac{\kappa^2}{\left[ S_{33}(\vec{q}, \dd) + \left| S_{33}(\vec{q}, \dd') \right| \right]} \\
M_{\text{T\perp}}^2 &= \left[ R_{33}(\vec{q}, \cc) - \left| R_{33}(\vec{q}, \cc') \right| \right] - \frac{\kappa^2}{\left[ S_{33}(\vec{q}, \dd) - \left| S_{33}(\vec{q}, \dd') \right| \right]} \\
M_{\text{LO}}^2 &= \left[ R_{22}(\vec{q}, \cc) + \left| R_{33}(\vec{q}, \cc') \right| \right] - \frac{\kappa^2}{\left[ S_{22}(\vec{q}, \dd) + \left| S_{22}(\vec{q}, \dd') \right| \right]} \\
M_{\text{LA}}^2 &= \left[ R_{22}(\vec{q}, \cc) - \left| R_{22}(\vec{q}, \cc') \right| \right] - \frac{\kappa^2}{\left[ S_{22}(\vec{q}, \dd) - \left| S_{22}(\vec{q}, \dd') \right| \right]} 
\end{align*}
\]
In this direction \( \xi = \frac{q}{q_{\text{max}}} \) where \( q_{\text{max}} = \frac{2\pi}{\sqrt{3}} \) and \( q_{\xi} = 0 \), 
\( q_y = \frac{2\pi}{\sqrt{3}} \), \( q_z = 0 \) \((0 \leq \eta \leq 1)\).

(c) [1120] direction

\[
2M\omega_{L0}^2 = \left[ A_1 + B_1 + x_1 \right]^{c-c} - \frac{k^2}{\left[ A_1 + B_1 + x_1 \right]^{d-d}}
\]

\[
2M\omega_{LA}^2 = \left[ A_1 + B_1 - x_1 \right]^{c-c} - \frac{k^2}{\left[ A_1 + B_1 - x_1 \right]^{d-d}}
\]

\[
2M\omega_{T0}^2 = \left[ A_2 + B_2 + x_2 \right]^{c-c} - \frac{k^2}{\left[ A_2 + B_2 + x_2 \right]^{d-d}}
\]

\[
2M\omega_{TII}^2 = \left[ A_2 + B_2 - x_2 \right]^{c-c} - \frac{k^2}{\left[ A_2 + B_2 - x_2 \right]^{d-d}}
\]

\[
M\omega_{T0}^2 = \left[ R_{33}(\bar{q}, cc) + iR_{33}(\bar{q}, cc') \right] \frac{k^2}{\left[ S_{33}(\bar{q}, dd) + iS_{33}(\bar{q}, dd') \right]}
\]

\[
M\omega_{TII}^2 = \left[ R_{33}(\bar{q}, cc) - iR_{33}(\bar{q}, cc') \right] \frac{k^2}{\left[ S_{33}(\bar{q}, dd) - iS_{33}(\bar{q}, dd') \right]}
\]

where

\[
A_1 = \left[ R_{11}(\bar{q}, cc) + iR_{11}(\bar{q}, cc') \right]
\]

\[
B_1 = \left[ R_{22}(\bar{q}, cc) - iR_{22}(\bar{q}, cc') \right]
\]

\[
x_1 = f(A_1 - B_1)^2 + 4\phi_1^2 1/2
\]

\[
\phi_1 = I_m R_{12}(\bar{q}, cc) - I_m R_{12}(\bar{q}, cc')
\]
Similarly

\[ A_2 = |R_{11}(\vec{q}, \mathbf{cc}) - |R_{11}(\vec{q}, \mathbf{cc'})|] \]

\[ B_2 = |R_{22}(\vec{q}, \mathbf{cc}) + |R_{22}(\vec{q}, \mathbf{cc'})|] \]

\[ x_2 = \{(A_2 - B_2)^2 + 4\pi^2\}^{1/2} \]

\[ \phi_2 = \mathcal{I}_m R_{12}(\vec{q}, \mathbf{cc}) + \mathcal{I}_m R_{12}(\vec{q}, \mathbf{cc'}) \]

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

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

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

In the expressions (5.1), (5.2) and (5.3), \( M \) represents the ionic mass, suffixes L and T correspond to longitudinal and transverse modes while \( O \) and \( A \) stand for optical and acoustic modes respectively. c-c and d-d are symbols for core-core and shell-shell interactions.

5.3 Evaluation of Model Parameters

The present model involves in all ten parameters \( \alpha_{1c}, \alpha_{2c}, \alpha_{1s}, \alpha_{2s}, x_{2c}, x_{3c}, \beta_{2c}, \gamma_{3c}, k \) and the bulk modulus of elasticity for electron gas \( K_e \). For their evaluation we have used five elastic constants (equations 4.24-4.29), the equilibrium condition (4.36) and the following four dispersions relations related to parameters.
\[ M_{\text{TOL}}^2 (\Gamma_3^+) = 12(\beta_{2c} + \gamma_{3c}) + 9 \frac{c^2}{a^2} (X_{2c} + \frac{X_{3c}}{4}) + A_p (1 - P)(a_{33} + \mid b_{33} \mid) + k \]
\[- \frac{k^2}{A_p (a_{33} + \mid b_{33} \mid) + k} \]

\[ M_{\text{TAll}}^2 (M_4^+) = 2\alpha_{1c} + 8\beta_{2c} + 6X_{3c} + A_p (1 - P)(a_{11} - \mid b_{11} \mid) + k \]
\[- \frac{k^2}{2\alpha_{1s} + A_p (a_{11} - \mid b_{11} \mid) + k} \]

\[ M_{\text{TAll}}^2 (K_5^+) = \frac{9}{2} \alpha_{1c} + 6(\beta_{2c} + \gamma_{3c}) + 3(X_{2c} + X_{3c}) + A_p (1 - P)a_{11} + k - 3\sqrt{3} \alpha_{2c} \]
\[- \frac{k^2}{\frac{9}{2} \alpha_{1s} + A_p (a_{11} - 3\sqrt{3} \alpha_{2s} + k} \]

\[ M_{\text{TOL}}^2 (K_1^+) = \frac{9}{2} \alpha_{1c} + 6(\beta_{2c} + \gamma_{3c}) + A_p (1 - P)a_{11} + k - 2A_p (1 - P)\mid b_{11} \mid + 3\sqrt{3} \alpha_{2c} \]
\[- \frac{k^2}{\frac{9}{2} \alpha_{1s} + A_p (a_{11} - 2\mid b_{11} \mid) + 3\sqrt{3} \alpha_{2s} + k} \]

where \( \omega \) denotes the angular frequencies at \( \Gamma_3^+ \), \( M_4^+ \), \( K_5^+ \) and \( K_1^+ \) points. \( \Gamma_3^+ \) and \( M_4^+ \) are the zone centre and zone boundary points for TOL and TAll along [0110] direction while \( K_5^+ \) and \( K_1^+ \) are the boundary points of T1 and T2 branches along [1120] directions.
We have used the notations used by Herrings\textsuperscript{93} for designating various dispersion branches and zone boundary points (Table 5.1) and levels used for branches of dispersion curves (Table 5.2).

**Table 5.1 Zone centre and zone boundary points representation**

<table>
<thead>
<tr>
<th>Zone boundary</th>
<th>Point level</th>
<th>Branch</th>
<th>Zone boundary</th>
<th>Point level</th>
<th>Branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>$\Gamma^+_3$</td>
<td>LO</td>
<td>$\Gamma^+_5$</td>
<td>$M^+_1$</td>
<td>IA</td>
</tr>
<tr>
<td></td>
<td>$\Gamma^+_6$</td>
<td>TA</td>
<td></td>
<td>$M^-_2$</td>
<td>LO</td>
</tr>
<tr>
<td></td>
<td>$\Gamma^-_2$</td>
<td>TO</td>
<td></td>
<td>$M^+_3$</td>
<td>TOI</td>
</tr>
<tr>
<td></td>
<td>$\Gamma^+_2$</td>
<td>LA</td>
<td></td>
<td>$M^-_3$</td>
<td>TOII</td>
</tr>
<tr>
<td>$K$</td>
<td>$K_1$</td>
<td>$T_1$(TO II)</td>
<td>$M^+_4$</td>
<td>$T_1$(IA)</td>
<td>$A_1$</td>
</tr>
<tr>
<td></td>
<td>$K_2$</td>
<td>$T_4$(LO)</td>
<td>$M^-_4$</td>
<td>$T_4$(TA II)</td>
<td>$A_3$</td>
</tr>
<tr>
<td></td>
<td>$K_3$</td>
<td>$T_4$(TA II)</td>
<td>$A_1$</td>
<td>$T_2$(TA)</td>
<td>TA</td>
</tr>
<tr>
<td></td>
<td>$K_5$</td>
<td>$T_1$(IA)</td>
<td>$A_1$</td>
<td>$T_3$(TA)</td>
<td>TO</td>
</tr>
<tr>
<td></td>
<td>$K_6$</td>
<td>$T_2$(TO I)</td>
<td>$A_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Symmetry direction</td>
<td>Branches</td>
<td>Nature of polarisation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>----------</td>
<td>-----------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[0001] or ( \Delta )</td>
<td>( \Delta_1 )</td>
<td>LA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Delta_2 )</td>
<td>LO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Delta_5 )</td>
<td>TA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Delta_6 )</td>
<td>TO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[01(\bar{1})0] or ( \Sigma )</td>
<td>( \Sigma_1 )</td>
<td>LA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Sigma_2 )</td>
<td>LO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Sigma_3 )</td>
<td>TA(\uparrow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Sigma_4 )</td>
<td>TO(\uparrow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Sigma_4 )</td>
<td>TA(\uparrow\uparrow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Sigma_4 )</td>
<td>TO(\uparrow\uparrow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[11(\bar{2})0] or ( \Sigma \Sigma )</td>
<td>( T_1 )</td>
<td>LA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( T_1 )</td>
<td>LO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( T_1 )</td>
<td>TA(\uparrow\uparrow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( T_1 )</td>
<td>TO(\uparrow\uparrow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( T_2 )</td>
<td>TO(\downarrow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( T_3 )</td>
<td>TAL</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.4 Numerical Computations, Results and Discussion on Phonon Dispersion Relations of Rare Earth Metals

5.4.a Holmium

Holmium is a rare earth metal having hexagonal close packed structure. Its axial ratio \((c/a)\) is 1.57. This ratio is perhaps least among hcp metals. The outer electronic configuration is \(4f^{10}, 5d^1, 6s^2\).

Several workers have studied the phonon dispersion of holmium. The elastic constants of holmium have been measured by Salama et al.\(^94\) between 78 to 700 K and by Palmer and Lee\(^95\) in the temperature range 42 to 300 K. Recently experimental measurements of dispersion relations using inelastic scattering of thermal neutrons have been done by Nicklow et al.\(^20\).

Lahteenkorva\(^96\) have studied the phonon dispersion of holmium using six neighbour axially symmetric model. In his model some artificial constraints have also been taken. The results compared well with the data of Leeke et al.\(^97\) in \([0001]\) direction but much deviation in \([01\overline{1}0]\) direction has been found. A theoretical mixed force model using least square fit technique for evaluation of force parameters has been used by Nicklow et al.\(^20\) to explain their own measured phonon dispersion curves. Sinha and Upadhyaya\(^98\) made a theoretical study of phonon dispersion in holmium considering five neighbour pairwise interaction on the lines of Krebs.\(^49\) The theoretical results were found in agreement with measured phonon data but as
they neglected the presence of many body interaction, their model is not satisfactory.

A phenomenological force constant model has been used by Sharma and Upadhyaya\textsuperscript{80}, taking three body forces on the lines of Roy et al\textsuperscript{99,100} in addition to usual forces of paired character to compute dispersion curves of Ho. The serious drawback of the their model is this that they neglected the electron ion interaction.

Recently\textsuperscript{82} a model for lattice dynamics of hcp metal Ho has been suggested which considers the non central interaction between the nearest neighbours of various arising from the overlap of spherical ions.\textsuperscript{81} The theoretical results show fairly good agreement with the experimental data on phonon dispersion.

**Present Study**

The present model has been also used to study the phonon dispersion of Holmium. In this model the interaction of an atom up to third nearest neighbours have been considered. The ten parameters are determined using all the five elastic constants at room temperature and four measured frequencies $\nu(T^3_3)$, $\nu(M^+_4)$, $\nu(K^+_1)$, $\nu(K^+_5)$ at zone centre and zone boundary points M and K. The experimental frequencies have been taken from the measurements of Nicklow et al.\textsuperscript{20}

The input data used in the evaluation of parameters are given in Tables 5.3 and 5.4.
Table 5.3 Frequencies and elastic constants used in the calculation for Holmium

<table>
<thead>
<tr>
<th>Frequencies at zone centre and zone boundary</th>
<th>Elastic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{12} Hz)</td>
<td>(10^{11} dyne/cm^2)</td>
</tr>
<tr>
<td>\nu(G^{-1}_3) = 3.40</td>
<td>C_{11} = 8.06</td>
</tr>
<tr>
<td>\nu(M^+_4) = 1.65</td>
<td>C_{12} = 2.84</td>
</tr>
<tr>
<td>\nu(K^{-1}_1) = 3.13</td>
<td>C_{13} = 2.25</td>
</tr>
<tr>
<td>\nu(K^{-1}_5) = 2.50</td>
<td>C_{33} = 8.22</td>
</tr>
</tbody>
</table>

Table 5.4 Various other physical constants used in the calculations for Holmium

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Atomic mass (a.m.u.)</th>
<th>r_e (Å)</th>
<th>K_F (Å^{-1})</th>
<th>a_0 (Å)</th>
<th>ε</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5773</td>
<td>5.6158</td>
<td>164.93</td>
<td>1.3526</td>
<td>1.413</td>
<td>0.528</td>
<td>0.353</td>
</tr>
</tbody>
</table>

The calculated parameters using Tables 5.3 and 5.4 are listed in Table 5.5.

Table 5.5 Evaluated parameters in the unit of 10^3 dyne/cm

<table>
<thead>
<tr>
<th>\alpha_{1c}</th>
<th>\alpha_{2c}</th>
<th>\alpha_{1s}</th>
<th>\alpha_{2s}</th>
<th>\beta_{2c}</th>
<th>\gamma_{3c}</th>
<th>x_{2c}</th>
<th>x_{3c}</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.88</td>
<td>2.91</td>
<td>0.18</td>
<td>-0.39</td>
<td>0.317</td>
<td>-0.184</td>
<td>5.715</td>
<td>0.935</td>
<td>-0.33</td>
</tr>
</tbody>
</table>
The value of parameter electronic bulk modulus $K_e$ has been calculated from equation (4.36) and is found to be $-0.084 \times 10^{11}$ dyne/cm$^2$. These force constants have been used to solve the secular determinant for various wavevectors as discussed in Section 5.1.

The computed dispersion curves for $\text{Ho}$ along three symmetry directions [0001], [0110] and [1120] are plotted in Figure 5.1 where they have been compared with experimental results of Nicklow et al. 20

For comparison of our results with experimental phonon frequencies a Table 5.6 is given in which phonon frequencies only at zone centre and zone boundary points along [0001] and [0110] are listed in the unit of $10^{12}$ Hz.

Table 5.6 Phonon frequencies along [0001] and [0110] directions at boundary points

<table>
<thead>
<tr>
<th>Modes</th>
<th>Experimental results</th>
<th>Calculated results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>$\bar{\Gamma}$</td>
</tr>
<tr>
<td>$\Delta_1$ (LA)</td>
<td>0.00</td>
<td>2.56</td>
</tr>
<tr>
<td>$\Delta_2$ (LO)</td>
<td>3.45</td>
<td>2.56</td>
</tr>
<tr>
<td>$\Delta_5$ (TA)</td>
<td>0.00</td>
<td>1.34</td>
</tr>
<tr>
<td>$\Delta_6$ (TO)</td>
<td>1.94</td>
<td>1.34</td>
</tr>
<tr>
<td>$\Sigma_1$ (LA)</td>
<td>0.00</td>
<td>3.04</td>
</tr>
<tr>
<td>$\Sigma_1$ (LO)</td>
<td>1.94</td>
<td>3.08</td>
</tr>
<tr>
<td>$\Sigma_3$ (TOL)</td>
<td>3.45</td>
<td>3.05</td>
</tr>
<tr>
<td>$\Sigma_3$ (TAL)</td>
<td>0.00</td>
<td>1.96</td>
</tr>
<tr>
<td>$\Sigma_4$ (TAH)</td>
<td>0.00</td>
<td>1.65</td>
</tr>
<tr>
<td>$\Sigma_4$ (TOM)</td>
<td>1.94</td>
<td>2.65</td>
</tr>
</tbody>
</table>
FIG. 5.1 PHONON DISPERSION CURVES FOR HOLMIUM ALONG SYMMETRY DIRECTIONS.
The calculated results agree well with the experimental data. The maximum deviation in any of the branch is not exceeding 8%. It may be concluded that the present model free from most of the shortcomings of earlier models explains measured phonon dispersion curves and elastic constants with ten parameters only.

5.4b Terbium

Terbium crystallises into hcp structure with axial ratio (c/a) 1.581, which is less than the ideal value. It is a rare earth metal having outer electronic configuration 4f\(^8\), 5d\(^1\), 6s\(^2\).

Salama et al.\(^94\) measured the elastic constants for terbium in the temperature range 78-300 K. Houmann and Nicklow\(^21\) have measured the phonon dispersion in terbium at room temperature. The inelastic scattering of thermal neutron technique has been used by these workers. To interpret their measured values, these authors have used a mixed force model taking general tensor interactions up to fourth neighbours and axially symmetric interactions up to next four neighbours, with 22 parameters. They obtained a satisfactory resemblance between experimental and theoretical results. Moreover the elastic constants calculated from these parameters are in good agreement with measured values of Salama et al.\(^94\)

Upadhyaya and Verma\(^69\) have used seven neighbour central force and five neighbour pairwise force model including the electron ion interaction to study phonon
dispersion curves of Tb in [0001] and [01\bar{1}0] directions. There is fairly good agreement with experimental results with maximum deviation up to 10%.

Sinha and Upadhyaya\textsuperscript{98} studied the phonon dispersion of terbium using five neighbour pairwise interaction model which include long range electron ion interaction on the lines of Krebs\textsuperscript{49}. The model considers the equilibrium of ionic lattice in a medium of uniform electron gas and the two equilibrium conditions necessary for hcp structure. The calculated results are in good agreement with experimental points but the desired degeneracy at K point could not be explained by this model as they left the presence of multi-ion forces in their model.

Recently Sharma and Upadhyaya\textsuperscript{80} have studied the lattice dynamics of Tb using five neighbours and six neighbours pair potential and many body forces following the work of Roy et al.\textsuperscript{99} The model explains the degeneracy at K point zone boundary and the ordering of dispersion modes. The results in all are in good agreement with the experimental values. These authors neglected the presence of conduction electrons into consideration.

**Present Work**

In the present work we have studied the phonon dispersion taking interactions up to third nearest neighbour through the model discussed earlier. The ten parameters have been determined using experimentally measured frequencies $\nu(\Gamma_3^+), \nu(M_4^+), \nu(K_1^+)$ and $\nu(K_5^+)$ at zone centre
and zone boundary points $M$ and $K$ and the experimental values of elastic constants.

The input data for calculation of force constants are given in Tables 5.7 and 5.8.

Table 5.7 Elastic constants and frequencies of terbium used in the present calculations

<table>
<thead>
<tr>
<th>Elastic constants</th>
<th>Frequency at zone centre and zone boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(10^{12}$ dyne/cm$^2$)</td>
<td>$(10^{12}$ Hz)</td>
</tr>
<tr>
<td>$C_{11}$ = 0.6788</td>
<td>$\nu(\Gamma^+_3) = 3.25$</td>
</tr>
<tr>
<td>$C_{12}$ = 0.2432</td>
<td>$\nu(\Gamma^+_4) = 1.59$</td>
</tr>
<tr>
<td>$C_{13}$ = 0.2299</td>
<td>$\nu(K_1) = 2.86$</td>
</tr>
<tr>
<td>$C_{33}$ = 0.7225</td>
<td>$\nu(K_5) = 2.35$</td>
</tr>
<tr>
<td>$C_{44}$ = 0.2140</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.8 Various other physical constants used in the calculations for terbium

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Atomic mass (a.m.u.)</th>
<th>$r_e$ (Å)</th>
<th>$K_F$ (Å$^{-1}$)</th>
<th>$\sigma$</th>
<th>$a_0$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$c$</td>
<td>3.59</td>
<td>5.69</td>
<td>158.925</td>
<td>1.365</td>
<td>1.4057</td>
</tr>
</tbody>
</table>

The evaluated force constants are listed in Table 5.9.
Table 5.9 Force parameters in $10^3$ dyne/cm

<table>
<thead>
<tr>
<th>$\alpha_{1c}$</th>
<th>$\alpha_{2c}$</th>
<th>$\alpha_{1s}$</th>
<th>$\alpha_{2s}$</th>
<th>$\chi_{2c}$</th>
<th>$\chi_{3c}$</th>
<th>$\beta_{2c}$</th>
<th>$\gamma_{3c}$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.1</td>
<td>3.08</td>
<td>-0.034</td>
<td>0.04</td>
<td>4.7</td>
<td>0.93</td>
<td>-0.057</td>
<td>0.00</td>
<td>-0.133</td>
</tr>
</tbody>
</table>

The electronic bulk modulus $K_e$ has been calculated from equation (4.36) derived on the basis of equilibrium condition and Cauchy discrepancy. The value of $K_e$ is $0.036 \times 10^{11}$ dyne/cm$^2$.

The calculated model force parameter are as in Table 5.9 including $K_e$ have been used to compute the dispersion curves along the symmetry directions by equations (5.1), (5.2) and (5.3). The theoretical curves along with the experimental neutron data of Houmann and Nicklow$^{21}$ are shown in Figure 5.2.

For the comparison of our results with experimental results, phonon frequencies at boundary points along [0001] and [0110] are given in Table 5.10.

Our results are excellent in general except a remarkable discrepancy at $M_3^-$ and $M_3^+$ points where it is lower than the experimental data by 21.7% and 10.03% respectively.
FIG. 5.2 PHONON DISPERSION CURVES FOR TERBIUM ALONG SYMMETRY DIRECTIONS.
Table 5.10  Phonon frequencies of terbium in unit of \(10^{12}\) Hz

<table>
<thead>
<tr>
<th>Modes</th>
<th>Experimental results</th>
<th>Frequencies calculated by present theory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Gamma)</td>
<td>(A)</td>
</tr>
<tr>
<td>(\Delta_1) (LA)</td>
<td>0.00</td>
<td>2.32</td>
</tr>
<tr>
<td>(\Delta_2) (LO)</td>
<td>3.25</td>
<td>2.32</td>
</tr>
<tr>
<td>(\Delta_5) (TA)</td>
<td>0.00</td>
<td>1.25</td>
</tr>
<tr>
<td>(\Delta_6) (TO)</td>
<td>1.82</td>
<td>1.25</td>
</tr>
<tr>
<td>(\Sigma_1) (LA)</td>
<td>(\Gamma)</td>
<td>(M)</td>
</tr>
<tr>
<td>(\Sigma_1) (LO)</td>
<td>1.82</td>
<td>3.05</td>
</tr>
<tr>
<td>(\Sigma_3) (TA\perp)</td>
<td>0.00</td>
<td>1.75</td>
</tr>
<tr>
<td>(\Sigma_3) (TO\perp)</td>
<td>3.25</td>
<td>2.85</td>
</tr>
<tr>
<td>(\Sigma_4) (TA\parallel)</td>
<td>0.00</td>
<td>1.59</td>
</tr>
<tr>
<td>(\Sigma_4) (TO\parallel)</td>
<td>1.82</td>
<td>2.85</td>
</tr>
</tbody>
</table>

The plasma frequency \(\nu_p\), given by \(\nu_p^2 = \frac{e^2 Z n^2}{8 \pi m}\) is sometimes used as a normalizing frequency for comparing the dynamical properties of different metals. Here \(Z\) is the valence, \(m\) is the mass and \(n\) is the number of atoms per unit volume. If the dynamics of Tb and Ho could be described by Coulomb interactions between positive ions embodied in a uniform negative charge, the normalised frequencies for these metals would be equal or since \(\nu_p\) is the same for Ho and Tb, the measured frequency would be
equal. However, as illustrated in the Tables 5.6 and 5.10, the phonon frequencies for Ho are approximately higher than those for Tb. Thus although the dispersion relation for Ho is qualitatively very similar to that of Tb, significant differences exist which are perhaps related to difference in the interatomic forces of these two materials and not to the small differences in atomic mass and volume. It is expected that a systematic study of the dynamical properties of all rare earth metals eventually may be correlated to a systematic study of their electronic structure.

An aspect of the comparison between Ho and Tb is at present a little puzzling. Ho possesses a spiral\textsuperscript{101} magnetic structure over a much wider range than does Tb. Since this type of magnetic order can be related to the existence of parallel sheets of Fermi surface which are separated by $K_0$, the wavevector of this spiral, it was anticipated an easily detectable Kohn type of anomaly might exist in the phonon spectrum of Ho for $q = K_0$, even though very little evidence of one was found for Tb. This was not the case; only very little evidence of such anomaly was also found for Ho. However there may be anomalies at other wavevectors that were overlooked. In any case all such anomalies in Ho must be very small.
5.5 Numerical Computations, Results and Discussion on Phonon Dispersion Relations of Transition Metals

5.5a Zirconium

Zirconium is a transition metal belonging to IVth group of periodic table with configuration $4s^2$, $p^6$, $d^2$, $5s^2$. The axial ratio is 1.593 which is less than the ideal value.

Pure zirconium atom solidifies at approximately 2123 K to a bcc structure ($\beta$-phase) and undergoes to a transformation of the martensitic type to a hcp structure ($\alpha$-phase) at about 1135 K. At low temperatures ($\leq 0.5$ K) zirconium becomes superconducting. For superconducting hcp transition elements room temperature measurements of dispersion curves indicate that there is correlation between the superconducting transition temperature $T_c$ and the anomalous behaviour of the zone centre [0001] $\Gamma\Omega$ mode.

The elastic constants of zirconium were measured by Fisher and Renken. The neutron inelastic scattering data of phonon dispersion were made available by Bezdek et al. These authors tried to interpret their measured phonon frequencies by modified axially symmetric (MAS) model involving thirteen independent parameters evaluated from neutron scattering data. Except for $\Sigma_1$ (LA) and $\Sigma_1$ (LO) modes at M point where discrepancies are 11% and 5% respectively there is satisfactory agreement in other modes with neutron measured data. Recently Stassis et al using inelastic neutron scattering technique determined the phonon spectra of hcp Zr along symmetry directions.
at 295 K, 773 K and 1007 K. It was observed that as temperature decreases a rather large increase in frequencies of all but the [0001] LO branch for which they have given the explanation of microscopic theory of lattice dynamics.

Kushwaha\textsuperscript{103} studied the lattice dynamics of zirconium taking interactions up to 5th neighbour. In his model six parameters are used. These parameters have been determined by one frequency and five experimental elastic constants with a slight modification in the value of $C_{44}$ for better adjustment with experimental results.

A new expression for electron interaction by averaging Bhatia's expression for the force at the ionic centres over the whole Wigner-Seitz sphere was obtained by Bajpai\textsuperscript{104} taking the central interaction up to fourth neighbour on the lines of Born-von Karman. The dispersion curves in [0001] and [0110] directions have been studied. Singh et al\textsuperscript{105} suggested an electron gas model for lattice dynamics of Zr. In their results near and at M point some of the branches exhibit a significant divergence from the experimental results.

Cavalheiro and Shukla\textsuperscript{106} extended the de Launay model for the lattice dynamics of Zr, Tb, Ho by immersing the point ion hcp lattice into free electron gas and calculating the electron-ion interaction. The calculated phonon dispersion curves along the principal symmetry directions are found to be in good agreement with the experimental results.
Vibhuti and Verma on the basis of a new model introducing non-central interaction between nearest neighbours of different type, studied the phonon dispersion curves of zirconium with reasonably good agreement with experimental results.

The drawback in all these models was that the long range matrix elements corresponding to atoms belonging to non-basal planes was deliberately taken to be zero which is not the real situation.

Recently Wakabayashi et al using their phenomenological charge fluctuation model analysed the phonon data for hcp zirconium. They found softening of the longitudinal [0001] LO near zone centre and interpreted as an incipient instability in the electronic system towards formation of a dipole charge density wave.

**Present Work**

In the present study the value of electronic bulk modulus and all other force constants have been determined using all the five experimental elastic constants and measured frequencies $v(T_3^+)$, $v(M_4^+)$, $v(K_1)$ and $v(K_5)$ at zone centre and zone boundary points M and K. The interaction of an atom up to third neighbour has been considered. The input data for calculation of force constants are given in Tables 5.11 and 5.12.
Table 5.11 Elastic constants and frequencies of zirconium used in the present calculation

<table>
<thead>
<tr>
<th>Elastic constants ((10^{11} \text{ dyn/cm}^2))</th>
<th>Experimental frequencies ((10^{12} \text{ Hz}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_{11}) = 14.35</td>
<td>(\nu(T^+_3)) = 2.5</td>
</tr>
<tr>
<td>(c_{12}) = 7.25</td>
<td>(\nu(M^+_4)) = 4.55</td>
</tr>
<tr>
<td>(c_{13}) = 6.54</td>
<td>(\nu(K_1)) = 4.30</td>
</tr>
<tr>
<td>(c_{33}) = 16.49</td>
<td>(\nu(K_5)) = 3.86</td>
</tr>
<tr>
<td>(c_{44}) = 3.207</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.12 Few more constants used in the calculations for zirconium

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Atomic mass (a.m.u.)</th>
<th>(r_e) (Å)</th>
<th>(K_F) (Å⁻¹)</th>
<th>(\sigma)</th>
<th>(a_0)</th>
<th>(P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2331</td>
<td>5.1491</td>
<td>91.22</td>
<td>1.5068</td>
<td>1.207</td>
<td>0.353</td>
<td>0.528</td>
</tr>
</tbody>
</table>

The electronic bulk modulus \(K_e\) has been calculated by equation (4.36) and its value found to be \(-0.0752 \times 10^{11}\) dyne/cm².

The other evaluated force constants for zirconium are given in the Table 5.13.
Table 5.13  Calculated force constants in $10^3$ dyne/cm$^2$

<table>
<thead>
<tr>
<th>$\alpha_{1c}$</th>
<th>$\alpha_{2c}$</th>
<th>$\alpha_{1s}$</th>
<th>$\alpha_{2s}$</th>
<th>$\beta_{2c}$</th>
<th>$\gamma_{3c}$</th>
<th>$x_{2c}$</th>
<th>$x_{3c}$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>-0.126</td>
<td>-0.349</td>
<td>-0.55</td>
<td>-1.649</td>
<td>0.586</td>
<td>9.817</td>
<td>-0.187</td>
<td>-2.43</td>
</tr>
</tbody>
</table>

These force constants have been used to solve the secular determinant for various wavevectors. The computed dispersion curve along symmetry directions have been shown in Figure 5.3 where they have been compared with experimental results$^{24}$ of Stassis et al.

For comparison of our results with experimental frequencies$^{26}$ a Table 5.14 is given in which phonon frequencies only at zone centre and zone boundaries along [0001] and [0110] directions in the unit of $10^{12}$ Hz are listed.

The anomalous behaviour of LO mode along [0001] direction could be obtained only within the framework of microscopic theory of lattice dynamics. Although in the last few years a considerable progress has been achieved in this direction, a microscopic theory suitable for realistic calculations at finite temperature is not presently available. The present model give satisfactory description of all modes along symmetry directions.
FIG. 5.3 PHONON DISPERSION CURVES FOR ZIRCONIUM ALONG SYMMETRY DIRECTIONS.
Table 5.14  Phonon frequencies of zirconium

<table>
<thead>
<tr>
<th>Mode of polarisation</th>
<th>Experimental results</th>
<th>Calculated results from present model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10^{12} Hz)</td>
<td>(10^{12} Hz)</td>
</tr>
<tr>
<td></td>
<td>[ \Gamma ]</td>
<td>[ A ]</td>
</tr>
<tr>
<td>( \Delta_1 ) (LA)</td>
<td>0.00</td>
<td>3.96</td>
</tr>
<tr>
<td>( \Delta_2 ) (LO)</td>
<td>4.55</td>
<td>3.95</td>
</tr>
<tr>
<td>( \Delta_5 ) (TA)</td>
<td>0.00</td>
<td>1.85</td>
</tr>
<tr>
<td>( \Delta_6 ) (TO)</td>
<td>2.61</td>
<td>1.85</td>
</tr>
<tr>
<td>( \Sigma_1 ) (LA)</td>
<td>0.00</td>
<td>5.29</td>
</tr>
<tr>
<td>( \Sigma_1 ) (LO)</td>
<td>2.61</td>
<td>5.74</td>
</tr>
<tr>
<td>( \Sigma_3 ) (TAI)</td>
<td>0.00</td>
<td>2.8</td>
</tr>
<tr>
<td>( \Sigma_3 ) (TOT)</td>
<td>4.55</td>
<td>4.94</td>
</tr>
<tr>
<td>( \Sigma_4 ) (TAA)</td>
<td>0.00</td>
<td>2.61</td>
</tr>
<tr>
<td>( \Sigma_4 ) (TOL)</td>
<td>2.61</td>
<td>4.64</td>
</tr>
</tbody>
</table>
5.5b Yttrium

The conduction-electron band structure of yttrium known to be transition-metal-like, in the sense that it consists of overlapping s-like and d-like bands. Its axial ratio \(c/a\) is 1.624. This ratio is close to the ideal axial ratio 1.633, showing the forces between the close packed planes are stronger than the forces within the planes.

Several workers have studied the lattice dynamical properties of yttrium. The elastic constants of yttrium have been determined by Smith and Gjevere\textsuperscript{109} in the temperature limit 4.2-400 K. Sinha et al\textsuperscript{25} measured the phonon dispersion curves along the three symmetric directions. They interpreted their results by MAS model with seventeen parameters determined by experimental elastic constants and neutron data. Except TA\textsubscript{1} branch in [01\overline{1}0] direction where deviation is 15%, the results agreed well with measured data.

Lahteencorva\textsuperscript{96} calculated the dispersion curves of yttrium using axially symmetric model based on the idea of quasi-elastic effective forces between the atoms. There is satisfactory agreement between the experimental and calculated results but at M point the frequencies deviate by 16%.

A non central force model of transition hcp metals have been proposed by Kushwaha and Kumar.\textsuperscript{110} The effect of conduction electrons is taken into account
on the lines of Krebs work. The calculated results on phonon dispersion are comparable with results measured.

Bajpal\textsuperscript{104} calculated the phonon dispersion relation of yttrium taking the central interaction up to fourth neighbour. Upadhyaya and Verma\textsuperscript{70} taking modified Sharma and Joshi electron-ion interaction term and five neighbour central pair potential obtained a reasonably good agreement with experimental results.

Rajput and Kushwaha\textsuperscript{111} calculated the phonon dispersion of yttrium with six parameters to explain measured results.

Cavalheiro and Shukla\textsuperscript{112} have calculated the phonon dispersion curves of yttrium along [0001] and [01\overline{1}0] directions with close resemblance with experimental results.

Menon and Rao\textsuperscript{113} used Keating approach to calculate phonon dispersion relations of yttrium. Kulshrestha\textsuperscript{114} and Upadhyaya used Animalu model potential approach to compute the dispersion curves of yttrium with good success.

Singh and Prakash\textsuperscript{115} considered the effect of d-electrons on the phonon frequencies of yttrium using isotropic non-interacting band models which are constructed with the help of energy band structure.

Wakabayashi et al\textsuperscript{108} in the analysis of phonon data of yttrium used a theoretical model (charge fluctuation model). It was found that data could be satisfactorily analysed in terms of a third Born-von Karman model without any charge fluctuation term.
Present Study

We have used our model which is free from common shortcomings of phenomenological models, to study phonon dispersion relations in yttrium. The force constants have been evaluated using all five elastic constant relations, two experimental frequencies $\nu(\Gamma_3^+)$ and $\nu(M_4^+)$. As the experimental frequencies of K point for T0M and TAW are not available, $\alpha_{2c}$ has been calculated from the following condition:

$$- I_m[R_{12}(\vec{q}, \text{cc}) + S_{12}^{-1}(\vec{q}, \text{dd})K] = I_m[R_{12}(\vec{q}, \text{cc'})]$$

$$+ S_{12}^{-1}(\vec{q}, \text{dd'})K]$$

and

$$- I_m[R_{12}(\vec{q}, \text{cc}) + S_{12}^{-1}(\vec{q}, \text{dd})K] = R_e[R_{11}(\vec{q}, \text{cc'})]$$

$$+ S_{12}^{-1}(\vec{q}, \text{dd'})K]$$

$I_m$ and $R_e$ are imaginary and real parts respectively. The force constant $\alpha_{2s}$ being small has been neglected in the present calculation.

The calculated force constants are listed in Table 5.17 while other constants used in the calculation for yttrium are given in Tables 5.15 and 5.16.

Table 5.15  Constants used in the calculation for yttrium

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Atomic mass (a.m.u.)</th>
<th>$r_e$ (Å)</th>
<th>$K_F$ (Å$^{-1}$)</th>
<th>$\sigma$</th>
<th>$a_0$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$c$</td>
<td>3.647</td>
<td>5.73</td>
<td>88.906</td>
<td>1.736</td>
<td>1.1009</td>
</tr>
</tbody>
</table>
Table 5.16  Frequencies and elastic constants of yttrium used in the present calculation

<table>
<thead>
<tr>
<th>Frequencies at zone centre and zone boundary (10^{12} Hz)</th>
<th>Elastic constants (10^{11} dyne/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu (\Gamma_{3}^+) = 4.64 )</td>
<td>( C_{11} = 7.790 )</td>
</tr>
<tr>
<td>( \nu (M_{4}^+) = 2.30 )</td>
<td>( C_{12} = 2.850 )</td>
</tr>
<tr>
<td></td>
<td>( C_{13} = 2.160 )</td>
</tr>
<tr>
<td></td>
<td>( C_{33} = 7.690 )</td>
</tr>
<tr>
<td></td>
<td>( C_{44} = 2.431 )</td>
</tr>
</tbody>
</table>

Table 5.17  Calculated force constants in the unit of 10^3 dyne/cm

<table>
<thead>
<tr>
<th>( \alpha_{1c} )</th>
<th>( \alpha_{2c} )</th>
<th>( \alpha_{1s} )</th>
<th>( \alpha_{2s} )</th>
<th>( \beta_{2c} )</th>
<th>( \gamma_{3c} )</th>
<th>( X_{2c} )</th>
<th>( X_{3c} )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.97</td>
<td>1.2847</td>
<td>0.097</td>
<td>0.00</td>
<td>0.431</td>
<td>-0.309</td>
<td>5.36</td>
<td>0.91</td>
<td>-0.188</td>
</tr>
</tbody>
</table>

The electronic bulk modulus of electron gas used as a parameter has been calculated from equation (4.36) and its value is \(-0.0752 \times 10^{11}\) dyne/cm^2 for yttrium. These force constants and \( K_{e} \) have been used to solve secular determinant for various wavevectors. The computed dispersion curves along with experimental data of Sinha et al.\(^{25}\) are shown in Figure 5.4.

It is found that at \( \Gamma_{6}^-, \ A_{3}^-, \ M_{3}^+; \ M_{3}^- \) points the theoretical results are lower by 1.5%.
FIG. 5.4 PHONON DISPERSION CURVES FOR YTTRIUM ALONG SYMMETRY DIRECTIONS.
respectively from experimental results. However at $M_4^+$, $M_4^-$ and $M_4$ the calculated results are 3.0%, 3.0% and 2.7% higher than neutron data.

Calculated results on phonon dispersion relations in case of yttrium agreeing well with the experimental data for all the branches except $T_{01}$ along $\Sigma$ direction where discrepancy of the order of 5% is observed at the $M$ point.

5.5c Hafnium

Hafnium is a transition metal which falls in IVth group of sixth period of the periodic table. Its $c/a$ ratio is 1.58 which is less than the ideal ratio 1.633 although the departure is not very large.

Earlier the phonon dispersion of hafnium have been studied by several workers. Fisher and Renken\textsuperscript{102} made a thorough investigations on the elastic constants of hafnium and have determined these constant at various temperatures in the range 4-1155 K. Using neutron scattering technique, lattice dynamics of hcp hafnium has been studied as regards dispersion curves along [0001], [0110] and [1100] symmetry direction by Stassis et al\textsuperscript{22} at 295 and 1300 K. As the temperature decreases the authors observed a rather large increase in the frequencies of all but [0001] $\Gamma$ branch. The zone centre mode of the [0001] $\Gamma$ branch on the other hand softens appreciably and at room temperature or low temperature this branch exhibits a dip at the zone centre. Liu et al\textsuperscript{116} suggested that the anomalous
behaviour of LO phonons is caused by splitting of doubly degenerate electronic branches nearby the Fermi level by lattice distorsion corresponding to the zone centre [0001] LO mode.

Wakabayashi et al.\textsuperscript{108} analysed the phonon data of Hf by presenting a phenomenological charge fluctuation model. These authors explained the softening of LO near due to incipient instability in the electronic system towards the formation of a dipolar charge density wave.

Kushwaha and Kumar\textsuperscript{110} by their non central force model calculated the dispersion relations of hafnium. In their work the dynamical matrix splits into two parts, one close shell part and other electronic part. The effect of electron gas is incorporated phenomenologically using Krebs approach.

Recently Saxena and Rathore\textsuperscript{83} presented a seven parameter model for hcp hafnium which assumes the (a) coupling between first, second and third neighbouring ions through a central pairwise potential, (b) the volume interaction due to conduction electrons after modifying the scheme of Ramamurti and Neelkandan.\textsuperscript{84}

**Present Study**

Using the model discussed in Chapter IV, the phonon dispersion have been calculated by taking interaction of an atom upto third nearest neighbour. The ten parameters have been determined using all the five elastic constants at room temperature and four measured frequencies
\( \nu(T^+), \nu(M^+_4), \nu(K_1^+) \) and \( \nu(K_5) \) at zone centre and zone boundary points \( M \) and \( K \). The experimental frequencies have been taken from the measurement of Stassis et al.\textsuperscript{22} while elastic constants from the work of Fisher and Renken.\textsuperscript{102}

The input data for the calculation of parameters are listed in Tables 5.18 and 5.19.

Table 5.18 Input data for hafnium: the elastic constants in unit of 10\textsuperscript{11} dynes/cm\textsuperscript{2} while frequencies in the unit of THZ

<table>
<thead>
<tr>
<th>Elastic constants</th>
<th>Experimental frequencies at zone centre and zone boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{11} ) = 19.01</td>
<td>( \nu(T^+)_3 ) = 3.1</td>
</tr>
<tr>
<td>( C_{12} ) = 1.45</td>
<td>( \nu(M^+_4) ) = 2.08</td>
</tr>
<tr>
<td>( C_{13} ) = 6.55</td>
<td>( \nu(K_1) ) = 3.55</td>
</tr>
<tr>
<td>( C_{33} ) = 20.44</td>
<td>( \nu(K_5) ) = 3.3</td>
</tr>
<tr>
<td>( C_{44} ) = 6.00</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.19 Other constants used in the calculations for hafnium

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Atomic mass (a.m.u.)</th>
<th>( r_e ) (Å)</th>
<th>( K_F ) (Å\textsuperscript{-1})</th>
<th>( \sigma )</th>
<th>( a_0 ) (Å)</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) = 3.1946</td>
<td>( c ) = 5.05</td>
<td>170.49</td>
<td>1.0998</td>
<td>1.723</td>
<td>0.353</td>
<td>0.528</td>
</tr>
</tbody>
</table>

The electronic bulk modulus \( K_e \) as calculated by equation (4.36) is \( 0.125 \times 10^{11} \) dyne/cm\textsuperscript{2} while 9 other parameters calculated from constants are given in Table 5.20.
Table 5.20 Evaluated parameters in the unit of $10^3$ dyne/cm

<table>
<thead>
<tr>
<th>$\alpha_{1c}$</th>
<th>$\alpha_{2c}$</th>
<th>$\alpha_{1s}$</th>
<th>$\alpha_{2s}$</th>
<th>$\alpha_{3c}$</th>
<th>$x_{2c}$</th>
<th>$x_{3c}$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.9</td>
<td>12.58</td>
<td>0.209</td>
<td>0.306</td>
<td>-7.446</td>
<td>7.272</td>
<td>11.987</td>
<td>2.281</td>
</tr>
</tbody>
</table>

These force constants have been used to solve secular determinant for various wavevectors. The computed dispersion curves along [0001], [0110] and [1120] directions are shown in Figure 5.5. The experimental points due to Stassis et al.\textsuperscript{22} are also shown for comparison.

For comparison the calculated frequencies from our model and experimental frequencies along [0001] and [0110] directions at zone centre and zone boundary points A and M are listed in the Table 5.21.

Table 5.21 Frequencies for hafnium in the unit of $10^{12}$ Hz

<table>
<thead>
<tr>
<th>Modes</th>
<th>Experimental results</th>
<th>Results from the model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>$A$</td>
</tr>
<tr>
<td>$\Delta_1$ (IA)</td>
<td>0.00</td>
<td>3.4</td>
</tr>
<tr>
<td>$\Delta_2$ (LO)</td>
<td>3.1</td>
<td>3.4</td>
</tr>
<tr>
<td>$\Delta_5$ (TA)</td>
<td>0.00</td>
<td>1.9</td>
</tr>
<tr>
<td>$\Delta_6$ (TO)</td>
<td>2.7</td>
<td>1.9</td>
</tr>
<tr>
<td>$\Sigma_1$ (IA)</td>
<td>0.00</td>
<td>3.8</td>
</tr>
<tr>
<td>$\Sigma_1$ (LO)</td>
<td>2.7</td>
<td>4.3</td>
</tr>
<tr>
<td>$\Sigma_4$ (TA)</td>
<td>0.00</td>
<td>2.14</td>
</tr>
<tr>
<td>$\Sigma_4$ (TO)</td>
<td>2.7</td>
<td>3.35</td>
</tr>
<tr>
<td>$\Sigma_3$ (TA)</td>
<td>0.00</td>
<td>2.4</td>
</tr>
<tr>
<td>$\Sigma_3$ (TO)</td>
<td>2.7</td>
<td>3.35</td>
</tr>
</tbody>
</table>
FIG. 5.5 PHONON DISPERSION CURVES FOR HAFNIUM ALONG SYMMETRY DIRECTIONS.
Our model gives an adequate description of the behavior of phonons in hafnium and observed anomalous behavior of LO branch at the zone centre along [0001] direction at room temperature.

5.5.d Scandium

Scandium is a transition metal belonging to third group of the periodic table. The ratio of lattice parameters c to a, called axial ratio is 1.59 less than the ideal value 1.632 for hcp structure. It is the lightest element with an outer electronic configuration (3d\(^1\) 4s\(^2\)) similar to those of rare earth metals. Energy band calculations have established that the conduction electron band structure and Fermi surface geometry of scandium are very like those for yttrium (4d\(^1\) 5s\(^2\)) and the heavy rare earth metals (5d\(^1\) 6s\(^2\)).

The elastic constants of scandium have been measured by Fisher and Dever\(^{117}\) while the lattice parameter by Gschneidner.\(^{118}\)

Wakabayashi et al.\(^{27}\) measured the phonon dispersion relations along the principal symmetry axes of hexagonal close packed metal scandium at room temperature by means of inelastic neutron scattering. These results have been analysed in terms of sixth neighbour modified axially symmetric force constant model. The anomaly has been found in \(\Delta_{LO}\) branch reflecting the nesting feature of the Fermi surface along that direction. Wakabayashi et al.\(^{108}\) analysed further the dispersion
data with a third Born-von Karman model without any charge fluctuation term. These authors also gave explanation for softening of [0001] \( \text{LO} \).

Upadhyaya and Verma \(^{119}\) studied phonons of scandium on the basis of modified Sharma-Joshi model with interaction extending to 17th neighbour. The results show varying degree of deviation from the experimental data corresponding to [01\( \bar{1} \)0] symmetry directions but the agreement in [0001] was found to be good.

Cavalheiro and Shukla \(^{106}\) extended the de-Launay model for lattice dynamics of scandium by immersing the point ion hcp lattice into a free electron gas and calculating the electron-ion interaction. These authors calculated the phonon dispersions along symmetry directions.

Singh and Prakash \(^{115}\) studied phonon dispersion considering effect of d-electrons on hcp transition metal scandium by their isotropic non interacting energy band model constructed with the help of energy band structure.

Saxena et al \(^{120}\) on the basis of earlier model of Vibhute and Verma \(^{81}\) introduced a non central interaction between nearest neighbours of different types arising from overlap of spheroidal ions to study dispersion relations of scandium. The agreement was found to be generally good.

Present Study

In the present model the interaction of an atom is considered upto third nearest neighbour. The force
constants have been evaluated using all five elastic constants relations and two experimental frequencies \( \nu(I_3^+) \) and \( \nu(M_4^+) \). As the experimental frequencies at K points for TA\parallel and TO\parallel are not available, the force constant \( a_{2c} \) has been calculated from the following conditions at zone boundary K point.

\[
- \text{Im}[R_{12}(q, cc)] + S_{12}^{-1}(q, dd)K = \text{Im}[R_{12}(q, cc')]
\]

\[
+ S_{12}^{-1}(q, dd')K]
\]

and

\[
- \text{Im}[R_{12}(q, cc)] + S_{12}^{-1}(q, dd)K = \text{Re}[R_{12}(q, cc')]
\]

\[
+ S_{12}^{-1}(q, dd')K]
\]

\( \text{Im} \) and \( \text{Re} \) are imaginary and real parts respectively. The force constant \( a_{2s} \) being very small has been taken to be zero in the present calculation.

The experimental frequencies are taken from the work of Wakabayashi et al.\(^{27}\) whereas the elastic constants are from the measurement of Fisher and Dever.\(^{117}\) The input data for the calculation of force constants are given in the Tables 5.22 and 5.23.

Table 5.22 Physical constants involving in the calculations for scandium

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Atomic mass (a.m.u.)</th>
<th>( r_e ) (Å)</th>
<th>( K_F ) (Å(^{-1}))</th>
<th>( \sigma )</th>
<th>( a_0 )</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>c</td>
<td>3.309</td>
<td>5.268</td>
<td>44.956</td>
<td>1.2575</td>
<td>1.5259</td>
</tr>
</tbody>
</table>
Table 5.23 The elastic constants and frequencies of scandium used in the present calculation

<table>
<thead>
<tr>
<th>Elastic constants (10^{11} \text{ dyne/cm}^2)</th>
<th>Frequencies at zone centre and zone boundary (10^{12} \text{ Hz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$ = 9.93</td>
<td>$\nu (\Gamma^{+}_{3})$ = 6.91</td>
</tr>
<tr>
<td>$C_{12}$ = 2.68</td>
<td>$\nu (M^{+}_{4})$ = 3.57</td>
</tr>
<tr>
<td>$C_{13}$ = 2.94</td>
<td></td>
</tr>
<tr>
<td>$C_{33}$ = 10.69</td>
<td></td>
</tr>
<tr>
<td>$C_{44}$ = 2.77</td>
<td></td>
</tr>
</tbody>
</table>

The calculated force constants in the unit of $10^3$ dyne/cm are given in Table 5.24.

Table 5.24 Calculated force constants ($10^3$ dyne/cm)

<table>
<thead>
<tr>
<th>$\alpha_{1c}$</th>
<th>$\alpha_{2c}$</th>
<th>$\alpha_{1s}$</th>
<th>$\alpha_{2s}$</th>
<th>$\beta_{2c}$</th>
<th>$\gamma_{3c}$</th>
<th>$X_{2c}$</th>
<th>$X_{3c}$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.00</td>
<td>1.916</td>
<td>-0.375</td>
<td>0.00</td>
<td>-1.461</td>
<td>1.406</td>
<td>6.704</td>
<td>0.054</td>
<td>-0.139</td>
</tr>
</tbody>
</table>

The parameter $K_e$ as calculated by equation (4.36) is found to be $0.039 \times 10^{11}$ dyne/cm$^2$.

These parameters have been used to solve dispersion relations along symmetry directions by equations (5.1), (5.2) and (5.3) for various wavevectors. The computed dispersion curves along [0001], [01\bar{1}0] and [11\bar{2}0] directions are shown in Figure 5.6. The experimental points
FIG. 5.6 PHONON DISPERSION CURVES FOR SCANDIUM ALONG SYMMETRY DIRECTIONS.
due to Wakabayashi et al.\textsuperscript{27} are also shown for comparison. The calculated frequencies for the present model and experimental frequencies along [0001] and [0\overline{1}\overline{1}0] directions at zone centre and zone boundary points are also listed in the Table 5.25 for comparison.

Table 5.25 Frequencies for scandium in the unit of $10^{12}$ Hz

<table>
<thead>
<tr>
<th>Modes</th>
<th>Experimental results</th>
<th>Theoretical results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>$A$</td>
</tr>
<tr>
<td>$\Delta_1$ (LA)</td>
<td>0.00</td>
<td>4.75</td>
</tr>
<tr>
<td>$\Delta_2$ (LO)</td>
<td>6.91</td>
<td>4.75</td>
</tr>
<tr>
<td>$\Delta_5$ (TA)</td>
<td>0.00</td>
<td>2.87</td>
</tr>
<tr>
<td>$\Delta_6$ (TO)</td>
<td>4.00</td>
<td>2.87</td>
</tr>
<tr>
<td>$\Sigma_1$ (LA)</td>
<td>0.00</td>
<td>6.21</td>
</tr>
<tr>
<td>$\Sigma_1$ (LO)</td>
<td>4.04</td>
<td>6.23</td>
</tr>
<tr>
<td>$\Sigma_4$ (TA\parallel)</td>
<td>0.00</td>
<td>3.6</td>
</tr>
<tr>
<td>$\Sigma_4$ (TO\parallel)</td>
<td>4.00</td>
<td>6.1</td>
</tr>
<tr>
<td>$\Sigma_3$ (TA\perp)</td>
<td>0.00</td>
<td>4.00</td>
</tr>
<tr>
<td>$\Sigma_3$ (TO\perp)</td>
<td>6.91</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Although calculated results are in good agreement with the experimental data along all the three symmetry directions, remarkable discrepancy of the order of 10% is observed in TO\parallel mode along $\Sigma$ direction.
5.5.e **Titanium**

Titanium is another transition metal which falls in fourth group of the periodic table. The axial ratio of titanium c/a is 1.59 (approximately), less than the ideal ratio 1.633 for hexagonal close packed structure.

In the case of titanium there is martensitic phase transition. The lattice dynamics of titanium is similar to that of zirconium and hafnium respectively. Larger decrease with increase in temperature in the frequencies of all but [0001] LO branch was observed. In this case again the zone centre mode of the [0001] LO branch soften's appreciably with decrease in temperature. Measurements of temperature dependence of the elastic constants of titanium have been performed by Fisher and Renken\(^\text{102}\) in the range (4-1155 K) and shown that decrease in the frequency with increasing temperature near \(q = 0\) is more pronounced for some branches than that observed in the present experiment for finite wavevector vibrational modes. This implies that the shifts in phonon frequencies are related to change in the long range interatomic forces which are mainly determined by the detailed electronic response to the nuclear motions. This suggests the temperature dependence of normal vibrational modes is closely related to the electronic structure near the Fermi line, play a dominant role in screening the nuclear motions and it is just these states which are strongly effected by changes in temperature.
The inelastic neutron scattering techniques have been used to study the lattice dynamics of hcp titanium by Stassis et al.\textsuperscript{23} The dispersion curves along symmetry directions are determined at 295, 773 and 1034 K.

Among the early workers Kushwaha and Kumar\textsuperscript{110} phenomenologically explained the dispersion relations of titanium taking the ionic and electron gas contribution to the dynamical matrix. Bajpai\textsuperscript{104} obtained an expression for electron-ion interaction by averaging Bhatia expression for the force at the ionic centres over the whole Wigner Seitz sphere. The author has taken the central interaction up to fourth neighbour using Born-von Karman method. However dispersion curves, only along two symmetry directions [0001] and [0110] have been obtained and compared to the experimental results.

**Present Study**

In the present work the interaction of an atom is considered up to third nearest neighbour. The force constants and bulk modulus of elasticity $K_e$ have been determined using all the elastic constants relations, equations (4.24 - 4.29) and four experimental frequencies $\nu(\Gamma_3^+)$, $\nu(M_4^+)$, $\nu(K_1)$ and $\nu(K_5)$ at zone centre and zone boundary points M and K. The experimental frequencies are taken from neutron scattering data of Stassis et al.\textsuperscript{23} at room temperature while elastic constants from the investigation of Fisher and Renken\textsuperscript{102}. The input data for the calculation of force constants are given in Tables 5.26 and 5.27.
Table 5.26  
Input data for titanium. The elastic constants in the unit of $10^{11}$ dyne/cm² while frequencies in the unit of THZ.

<table>
<thead>
<tr>
<th>Elastic constants</th>
<th>Frequencies at zone centre and zone boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$ = 17.61</td>
<td>$\nu(T_3^+)$ = 4.17</td>
</tr>
<tr>
<td>$C_{12}$ = 8.69</td>
<td>$\nu(M_4^+)$ = 3.5</td>
</tr>
<tr>
<td>$C_{13}$ = 6.83</td>
<td>$\nu(K_1)$ = 6.85</td>
</tr>
<tr>
<td>$C_{33}$ = 19.05</td>
<td>$\nu(K_5)$ = 6.00</td>
</tr>
<tr>
<td>$C_{44}$ = 5.08</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.27  
Various other physical constants involved in the calculation for titanium.

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
<th>Atomic mass (a.m.u)</th>
<th>$r_e$ (Å)</th>
<th>$K_F$ (Å⁻¹)</th>
<th>$\sigma$</th>
<th>$a_o$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$c$</td>
<td>2.9506</td>
<td>4.6788</td>
<td>47.90</td>
<td>1.0171</td>
<td>1.8791</td>
</tr>
</tbody>
</table>

The parameter $K_e$, the bulk modulus of elasticity for electron gas has been calculated from equation (4.36). Its value is $0.398 \times 10^{11}$ dyne/cm².

Nine other calculated force parameters are listed in Table 5.28.
Table 5.28 Calculated parameters for titanium in the units of $10^3$ dyne/cm

<table>
<thead>
<tr>
<th>$\alpha_{1c}$</th>
<th>$\alpha_{2c}$</th>
<th>$\alpha_{1s}$</th>
<th>$\alpha_{2s}$</th>
<th>$\beta_{2c}$</th>
<th>$\gamma_{3c}$</th>
<th>$X_{2c}$</th>
<th>$X_{3c}$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.23</td>
<td>1.17</td>
<td>1.6</td>
<td>2.65</td>
<td>1.281</td>
<td>-1.793</td>
<td>10.237</td>
<td>1.655</td>
<td>-3.1103796</td>
</tr>
</tbody>
</table>

These parameters have been used to solve dispersion relations (5.1), (5.2) and (5.3) for various wavevectors. The computed dispersion curves along [0001], [01\overline{1}0] and [11\overline{2}0] directions are shown in Figure 5.7. The experimental frequencies due to Stassis et al.\textsuperscript{23} are also shown for comparison.

For some more specific comparison with experimental data some of the frequencies at zone boundary and zone center points along [0001] and [01\overline{1}0] directions are shown in Table 5.29.

Table 5.29 Frequencies for titanium in the unit of $10^{12}$ Hz

<table>
<thead>
<tr>
<th>Modes</th>
<th>Experimental results</th>
<th>Theoretical results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>$\Lambda$</td>
</tr>
<tr>
<td>$\Delta_1$ (LA)</td>
<td>0.00</td>
<td>5.73</td>
</tr>
<tr>
<td>$\Delta_2$ (LO)</td>
<td>5.54</td>
<td>5.73</td>
</tr>
<tr>
<td>$\Delta_5$ (TA)</td>
<td>0.00</td>
<td>3.05</td>
</tr>
<tr>
<td>$\Delta_6$ (TO)</td>
<td>4.2</td>
<td>3.05</td>
</tr>
<tr>
<td>$\Sigma_1$ (IA)</td>
<td>0.00</td>
<td>7.1</td>
</tr>
<tr>
<td>$\Sigma_1$ (LO)</td>
<td>4.57</td>
<td>7.69</td>
</tr>
<tr>
<td>$\Sigma_4$ (TA II)</td>
<td>0.00</td>
<td>3.4</td>
</tr>
<tr>
<td>$\Sigma_4$ (TO II)</td>
<td>4.57</td>
<td>6.95</td>
</tr>
<tr>
<td>$\Sigma_4$ (TA I)</td>
<td>0.00</td>
<td>3.82</td>
</tr>
<tr>
<td>$\Sigma_3$ (TO I)</td>
<td>5.54</td>
<td>6.2</td>
</tr>
</tbody>
</table>
FIG. 5.7 PHONON DISPERSION CURVE FOR TITANIUM ALONG SYMMETRY DIRECTIONS.
Reasonably good agreement between calculated and observed phonon frequencies exhibit for all the branches except for TA1 and TO1 branches at large q values along [0110] direction. The anomalous behaviour of LO branch at zone centre along [0001] mode is also explained by the present model.

5.6 General Discussions

In general the phonon frequencies at K point in hcp metals like Ho and Tb do not follow the Warren sum rule i.e.

\[ 2v^2(K_5) = v^2(K_1) + v^2(K_3) \]

which applies for the central pairwise forces operative in a hcp system. Since the modified axially symmetric (MAS) model, and simple pseudopotential approach with second order perturbation term most commonly used to interpret the dispersion relations in hcp metals, describe the lattice dynamics essentially through two body type interactions cannot explain the phonon dispersion relations in hcp metals, particularly along [11\overline{2}0]. In these methods the matrix element \( I_m[D_{12}(\vec{q}_{11})] \) (\( = I_m[K_{12}(\vec{q}, cc) + S_{12}^{-1}(\vec{q}, dd)K] \)) is zero. But as shown by Roy et al. this term should not be zero in order to interpret the correct ordering of dispersion branches along [11\overline{2}0] direction. In the third order perturbation scheme of Bertoni et al. for hcp system and in the general force analysis the element \( I_m[D_{12}(\vec{q}_{11})] \) is non zero. Although these methods use
multi ion forces but their role is not seen directly.

In the present work we have developed a force constant model which incorporates the effect of conduction electrons on the line of Krebs. Unpaired forces however have been obtained using the character of general tensor force which give non zero value of matrix element $I_m[D_{12}(G_{11})]$. This scheme is able to produce asymmetric $\nu^2(K_1)$ and $\nu^2(K_3)$ frequencies with respect to $\nu^2(K_5)$. The presence of three body forces produce a desired ordering of phonon dispersion curves in $\Gamma K M$ directions for Ho, Tb, Zr, Y, Ti, Hf hcp metals. With the adjustment of three body force parameters $a_{1c}', a_{2c}', a_{1s}', a_{2s}$ to produce the correct values of $\nu(K_1)$, $\nu(K_3)$ and $\nu(K_5)$. This success provides a firm footing, of course in a phenomenological but simple way to the view that unpaired forces play an important role in the lattice dynamics of hcp metals.

The present study gives us an expression for the Cauchy discrepancy $C_{13} - C_{44}$ which is $4.4 K_e$ for hcp system. The complete equilibrium of hcp lattice in presence of pairwise as well as three body ion-ion and ion-electron interaction has been considered.