CHAPTER 3

3.1

BOND BENDING RIGID ION MODEL

The model employed in this study is the Bond Banding Rigid Ion Model (B.B.R.I.M.)

The theory of BBRIM basically incorporates the effect of bond-bending forces and the short-range repulsive forces including the third neighbors, in addition to the long-range columbic interaction. The general formulation of the BBRIM remains in the harmonic and adiabatic approximations and can be derived using the crystal potential energy expressed as following:-

$$\phi=\frac{1}{2}\sum_{I,K}\sum_{i'k'}\phi\left(|\,r(IK,I'K')|\right)+\frac{1}{2}\frac{e^2}{\nu}\gamma_\theta(\delta\theta)^2 + \frac{1}{2}\sum_{IK}\sum_{I'k'\neq Ik}\frac{Z_K Z_K e^2}{|\,rIK,I'k'|} \qquad \textbf{(3.1)}$$

Where first and third terms respectively, represent the short-range and long-range columbic interaction potentials. The second term represents the short-range interaction potential which gives rise to the bond-bending forces having three-body character (see figure **3.1**). In this term $(\delta\theta)$ is the change in the angle under consideration and γ_θ is the corresponding force constant. The change in the angle $\delta\theta$ is geometrically calculated using-

$$(\delta\theta)=\left(\frac{\left(\vec{S}_A-\vec{S}_O\right).\varepsilon_{nA}}{\left[\overrightarrow{OA}\right]}+\frac{\left(\vec{S}_B-\vec{S}_O\right).\varepsilon_{nB}}{\left[\overrightarrow{OB}\right]}\right) \qquad \textbf{(3.2)}$$

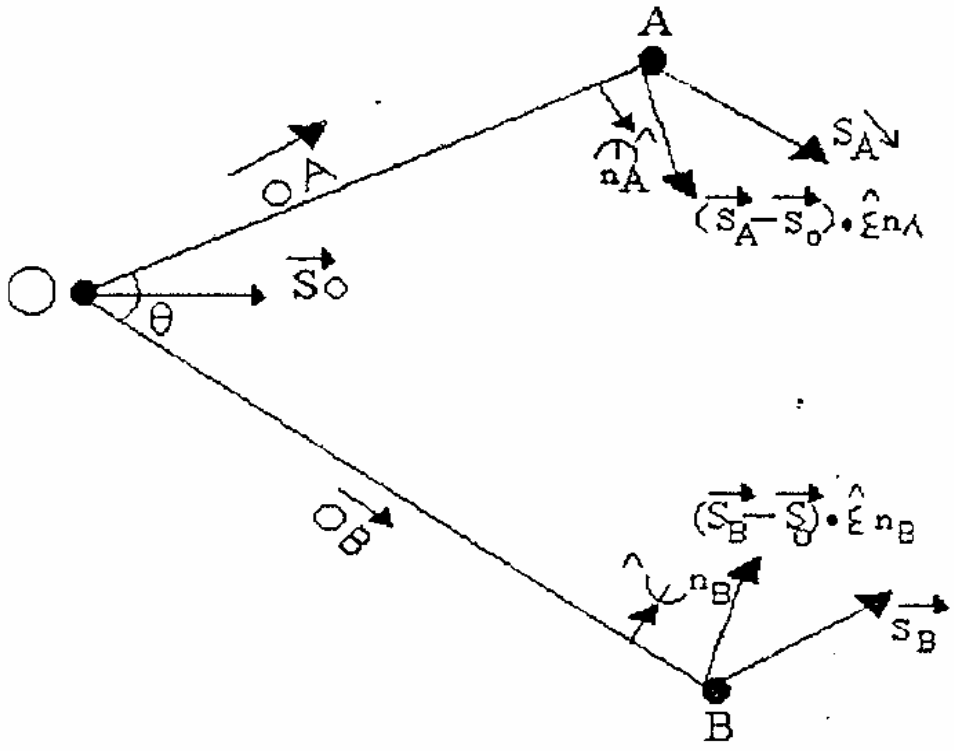

Figure 3.1 Clark Gazis Wallis (CGW) type angular forces

Where $\vec{S}_A$, $\vec{S}_o$ and $\vec{S}_B$ are displacement vectors of the respective atoms A, O and B. $\vec{\varepsilon}_{nA}$ and $\vec{\varepsilon}_{nB}$ are the unit vectors perpendicular to OA and OB, respectively, and are such that they always tend to reduce the angle AOB (figure 3.1)

The potential energy ϕ as given in equation can, therefore he split in two parts:

$$\phi = \phi^R + \phi^C \qquad \textbf{(3.3)}$$

ϕ^R stands for the short-range repulsive contribution and for the long-range Columbic contribution. Now we shall evaluate matrix elements for the short-range part embodying two-body (ϕ_1^R) and three body (ϕ_2^R) potential energies.

3.1.1 THE SHORT RANGE INTERACTION

In the present approach we shall consider two-body and three-body interaction for evaluating the short-range matrix elements.

3.1.2 THE TWO-BODY SHORT RANGE CONTRIBUTION

The potential energy for this part has been designated by ϕ_I^R and we shall expand this using Taylor's series:

$$\phi_I^R = \sum_{1mm}\left\{\frac{1}{r}\left(\frac{d\phi_i^R}{dr}\right)_{r=r_1}\left[r^\circ_{1mm}.(S_{1mm}-S_0)+\frac{1}{2}\left|S_{1mm}-S_0\right|^2\right]\right.$$
$$\left.+\frac{1}{2}\left(\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi_1^R}{dr}\right)\right)_{r=r_1}\left[r^\circ_{1mm}.(S_{1mm}-S_0)\right]^2\right\} \qquad \textbf{(3.4)}$$

r°_{1rnm} represents the position coordinates of neighboring atoms in equilibrium. The higher terms in the expansion of the Taylor's series have been neglected l, m, n represents the direction cosines of the line joining the central ion and it's nearest neighbor. r_1 is the nearest neighbor distance. The summation over equation **(3.4)** extends over the first three nearest

neighbors of the central ion at the origin. Earlier most of the authors have equated the first derivative $\left(\frac{d\phi_1^{rr}}{dr}\right)_{r=r_1}$ equal to zero. Actually this is not true because ϕ_1^r does not present this entire potential the determining equilibrium distance r_1.

3.1.3 THE THREE-BODY SHORT RANGE INTERACTION

As already mentioned earlier the second term in the potential energy expression 1/2 $\gamma_\theta (\delta\theta)^2$ is used to obtain matrix elements for fluorite as well as CdI_2 structure compounds. This part of potential energy is expressed by ϕ_2^R .

3.2

EXPRESSION FOR THE DYNAMICAL MATRICES OF FLUORITE STRUCTURE

The fluorite lattice consists of three interpenetrating due centered-cubic sub lattices with three atoms per unit cell. These sub lattices are occupied by one metal atom and two non equivalent fluorine atoms F and F_2.

The lattices of F_1 and F_2 are displaced along the body diagonal of the metal lattice by a (1/4, 1/4, 1/4,) and a (3/4, 3/4, 3/4) respectively, where a is the lattice constant (Figure **1.1**). Each metal atom is surrounded by four fluorine atoms F_1 and four fluorine atoms F_2, the eight atoms lying at the corners of a cube with metal atoms arranged in a tetrahedral fashion around it. Therefore, metal atom has 8 first nearest neighbours (at a distance of $\sqrt{3}$ a/4) and 12 second nearest neighbour (at a distance of $\frac{a}{\sqrt{2}}$). While the fluorine atom F_1 or F_2 has 4 first nearest neighbours (at a distance of $\frac{\sqrt{3a}}{4}$) six second nearest neighbors (at a distance of 1/2a) and twelve third nearest neighbors (at a distance $a/\sqrt{2}$). The coordinates of these neighbors are listed in table (**1.1**) and (**1.2**). The unit cell can be chosen as a rhombohedron of volume $a^3/4$ bounded by edges a_1=½a (001), a_2=1/2a(101) and a_2=½a (110).

3.2.1 THE TWO BODY SHORT-RANGE MATRIX ELEMENTS

In the present work we have expressed

$$B_k = \frac{1}{r}\left(\frac{d\phi_l^r}{dr}\right)_{r=r_k} \qquad \text{and} \qquad A_k = \left(\frac{d^2\phi_l^r}{dr^2}\right)_{r=r_k}$$

Where k = 1,2,3,4 first four nearest neighbors. Thus at the stage the present model involves 8 short range two body force constants (A_1, A_2, A_3 A_4 and B_1, B_2, B_3 B_4).

Matrix elements corresponding to two body short range interaction are obtained using coordinates of various atoms as given in the table. These elements are as follows

$$D_1^R\begin{bmatrix}1 & 1\\ x & x\end{bmatrix} = \frac{8}{3}(A_1 + 2B_1) + 2A_3\left[2 - C_{2x}\left(C_{2y} + C_{2z}\right)\right]$$

$$+ 2B_3\left[4 - \left\{2C_{2y}C_{2z} + C_{2x}\left(C_{2y} + C_{2z}\right)\right\}\right]$$

$$D_1^R\begin{bmatrix}1 & 1\\ x & x\end{bmatrix} = 2(A_3 - B_3)S_{2x}S_{2y}$$

$$D_1^R\begin{bmatrix}2 & 2\\ x & x\end{bmatrix} = \frac{4}{3}(A_1 + 2B_1) + 2(A_2 + 2B_2) - 2A_4C_{2x}\left(C_{2y} + C_{2z}\right) - 2B_4\left[2C_{2y}C_{2z} + C_{2x}\left(C_{2y} + C_{2z}\right)\right]$$

$$4(A_4\,2B_4)$$

$$D_1^R\begin{bmatrix}2 & 2\\ x & y\end{bmatrix} = 2(A_4 - B_4)S_{2x}S_{2y} \qquad \textbf{(3.5)}$$

$$D_1^R\begin{bmatrix}1 & 2\\ x & y\end{bmatrix} = -\frac{4}{3}(A_1 + 2B_1)\left(C_xC_yC_z - iS_xS_yS_z\right)$$

$$D_1^R\begin{bmatrix}2 & 4\\ x & y\end{bmatrix} = \frac{4}{3}(A_1 - B_1)\left(S_xS_yS_z - iC_xC_yC_z\right)$$

$$D_1^R\begin{bmatrix}2 & 4\\ x & x\end{bmatrix} = -2A_2C_{2x} - 2B_2\left(C_{2y} + C_{2z}\right)$$

$$D_1^R\begin{bmatrix}2 & 4\\ x & y\end{bmatrix} = 0$$

Where S_x=Sin ($aq_x/4$),C_x=Cos($aq_x/4$)

S_{2x}=Sin ($aq_x/2$),C_{2x}=Cos ($aq_x/2$)

It is to be remembered that matrix elements are Hermitian,

In literature, force constants A_k and B_K are similar to the angular and central force constants of De launay.

3.2.2 THE THREE BODY SHORT-RANGE MATRIX ELEMENTS:

The potential energy for this contribution is designated by ϕ_2^R this corresponds to the second term in equation **(3.1)** which read as

$$\phi_2^R = \frac{1}{2}\frac{e^2}{v}\gamma_0(\delta\theta)^2 \qquad \textbf{(3.6)}$$

Where $\bar{\delta}\theta$ is defined in equation **(3.2)**

In the derivatives of the expression for the fluorite structure be considered two types of triangular as shown in figure **1.1**, (1) triangles formed by the origin atom and two of its nearest neighbors for examples ABC, and (2) the second set of triangles formed by the atom at the origin, one of its nearest neighbors such as ABD. Each of these triangles are isosceles, they will involve two force constants each. Here γ_1 and γ_2 are the respective force constants associated with angles at A and B (or C) in the triangle ABC and γ_3 and γ_4 are the force constants associated with angles at B and A (or D) with triangles ABD respectively. Such type of force constants were introduced by Clark Gazis and Wallis (CGW)[32] for lattice dynamics studies. Matrix elements for three body short range interaction corresponding to the potential energy ϕ_2^R are follows:

$$D_2^R\begin{bmatrix}1 & 1\\ x & x\end{bmatrix} = 32k_1 + 48k_2 + 28k_3 - 2k_3C_{2x}\left(C_{2y} + C_{2z}\right)$$

$$+\left(8k_3 + 4k_4\right)C_{2y}C_{2z}$$

$$D_2^R\begin{bmatrix}1 & 1\\ x & y\end{bmatrix} = -\left(16k_1 + 24k_2 + 16k_3 + 16k_4\right)\left(C_xC_yC_z - iS_xS_yS_z\right)$$

$$D_2^R\begin{bmatrix}2 & 2\\ x & x\end{bmatrix} = 24k_1 + 36k_2 + 14k_3 + 14k_4 + \left(4k_3 + 2k_4\right)C_{2y}C_{2z} - k_3C_{2x}\left(C_{2y} + C_{2z}\right)$$

$$D_2^R\begin{bmatrix}2 & 2\\ x & y\end{bmatrix} = k_3S_{2x}S_{2y} + i2\left(k_3 + k_4\right)S_{2z}\left(C_{2x} - C_{2y}\right)$$

$$D_2^R\begin{bmatrix}1 & 2\\ x & x\end{bmatrix} = -\left(16k_1 + 24k_2 + 16k_3 + 16k_4\right)\left(C_xC_yC_z - iS_xS_yS_z\right)$$

$$D_2^R\begin{bmatrix}1 & 2\\ x & x\end{bmatrix} = -\left(8k_1 + 12k_2 + 8k_3\right)\left(S_xS_yS_z - iC_xC_yC_z\right)$$

$$D_2^R\begin{bmatrix}2 & 4\\ x & x\end{bmatrix} = -16k_1C_{2x} + \left(4k_1 - 6k_2\right)\left(C_{2y} + C_{2z}\right) \qquad \textbf{(3.7)}$$

$$D_2^R\begin{bmatrix}2 & 4\\ x & x\end{bmatrix} = -i\left(4k_1 + 6k_2\right)S_{2z}$$

Where we have put

$$\frac{8y_1}{9a^2} = k_1$$

$$\frac{2y_2}{9a^2} = k_2$$

$$\frac{32y_3}{9a^2} = k_3$$

$$\frac{24y_4}{9a^2} = k_4$$

Other coefficient can be derived by a cyclic inter change of x, y and z using the fact that the dynamical matrix is Hermitian. The following relations hold for the matrix elements.

$$D\begin{bmatrix} k & k^1 \\ x & y \end{bmatrix} = D\begin{bmatrix} k^1 & k \\ x & y \end{bmatrix}, \qquad D\begin{bmatrix} 1 & 4 \\ x & y \end{bmatrix} = D\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix},$$

$$D\begin{bmatrix} 2 & 2 \\ x & y \end{bmatrix} = D\begin{bmatrix} 4 & 4 \\ x & y \end{bmatrix},$$

C_x=Cos (aq_x/4), S_x=Sin (aq_x/4),

C_{2x}=Sin (aq_x/2), S_{2x}=Sin (aq_x/2),

Where 'a' is lattice constant.

3.2.3 MATRIX ELEMENTS FOR LONG-RANGE INTERACTION

The matrix elements for the long range Columbic interaction have been used for the 47 irreducible lattice vectors in 1/48 of the first Brillion zone of the reciprocal space to which a mesh of 1000 wave vector points reduces by symmetry consideration. Kellermann[66] has calculated the coefficients $D^C\begin{bmatrix} k & k \\ x & y \end{bmatrix}$ and $D^C\begin{bmatrix} 2 & 4 \\ x & y \end{bmatrix}$ for those 47 points, while Dayal and Tripathi[37] have computed $D^C\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix}$ at the same points. We have used these values with present work after multiplying them with $Z_2^2 e^2/V$. Here Z_2 is effective charge of the metal-ions (in unit of e) and V is the volume of unit cell. The matrix elements are as follows.

$$D^C\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} = \frac{e^2}{v}\left[-G_{xy}^{11} + H_{1xy} + \frac{8\varepsilon^3}{3\sqrt{\pi}}\delta_{xy}\right]$$

$$D^C\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix} = \frac{e^2}{v}\left[+G_{xy}^{12} - H_{mxy} + {}_{xy_m}\right]$$

Where

$$G_{xy}^{11} = 4\pi \sum_{h} \frac{(h_x + q_x)(h_y + q_y)}{|h+q|^2} \exp\left[-\frac{\pi 2}{4\varepsilon^n} (h+q)^2 \right]$$

$$G_{xy}^{12} = 4\pi \sum_{h} \frac{(h_x + q_x)(h_y + q_y)}{|h+q|^2} \exp\left[-\frac{\pi 2}{4\varepsilon^n} (h+q)^2 Cos(h_x + h_y + h_z) \right]$$

$$H_{lxy} = 2\sum_{1} \left[-f(1)\delta_{xy} + g(1)\frac{I_x I_y}{I^2} \right] Cos\pi(q.\bar{I}) \qquad \textbf{(3.8)}$$

$$f(1) = \frac{2\varepsilon}{\sqrt{\pi l^2}} \exp\left[-\varepsilon^2 1^2 \right] + \frac{\psi(\varepsilon 1)}{1^3}$$

$$g(1) = \frac{1\varepsilon^3}{\sqrt{\pi}} \exp\left[-\varepsilon^2 l^2 \right] + \frac{6\varepsilon}{\sqrt{\pi l^2}} \exp\left[-\varepsilon^2 l^2 \right] + \frac{3\psi(\varepsilon l)}{l^3}$$

$$\psi(\varepsilon l) = 1 - \frac{2}{\sqrt{\pi}} \int_{o}^{\varepsilon l} \exp\left[-\xi^2 \right] d\xi$$

$$l = |l| = \sqrt{\left(l_x^2 + l_y^2 + l_z^2 \right)}$$

$$h^2 = h_x^2 + h_y^2 + h_z^2$$

Where v is volume of the unit cell (rhombohedral) and e is the electronic charge, h_x, h_y, h_z cover all sets of integers which are either all odd or all even. Similarly l_x, l_y, l_z and m_x m_y and m_z are integers with condition that $\sum_x \ell_n$ = even and $\sum_x m_x$ = odd. The wave vector $\vec{q}$ is closely related to the wave vector $\vec{k} = \frac{1}{\lambda}$

3.3

EXPRESSION FOR THE DYNAMICAL MATRICES OF CdI_2 STRUCTURE

The CdI_2 structure is a layered structure of space group D. The individual tightly bounded layer in MX_2 (M=metal atom, X= chalcogenides atom) is an X-M-X sandwich and the adjacent sandwiches are held together along the c-axis by weak Van der Waals forces (Figure**1.3**) because the primary valencies of constituent atoms are almost fully satisfied within the layer. Each metal atom (M) is octahedrally coordinated (Figure**1.3a**) to six nearest neighbor X atoms. Each X atom is nested atop a triangle of M atoms. The stacking sequence along the c-axis is thus M-X-X-M, and the relatively weak X-X interaction results in the compound having layer like character (Figure**1.3b**). Thus unit cell spans only one layer and contains one molecular unit MX_2 i.e. three atoms. For our convenience, we assigned the lower layer chalcogen atom (X_1) as 1, the metal atom (M) as 2 and upper layer chalcogen atom (B_2) as 3.

We have expressed the total potential energy consisting of (1) the two-body short range component ϕ_1^r (2) the three body short range component ϕ_2^r , and the long-range columbic component ϕ^C Matrix elements for these contributed have been obtained using coordinates as listed in the tables (**1.4**), (**1.5**) and (**1.6**) for the CdI_2 structure.

3.3.1 THE TWO-BODY SHORT RANGE MATRIX ELEMENT

We have defined here first and second derivative of the potential energy as angular and central force constant of DeLaunay. Thus

$$B_k = \frac{1}{r}\left(\frac{d\phi_1^r}{dR}\right)_{r=r_1} \quad A_k = \left(\frac{d^2\phi_1^r}{dr^2}\right)_{r=r_1}$$

In this case due to complexity of the layered structure, we have con find ourselves to first and second nearest neighbors only. Four force constants A_1, A_2, B_1, B_2 shall appear in matrix elements. Matrix elements are as follows:

$$D_1^R\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ y & y \end{bmatrix} = 3B_1 + (a^2 / 2A^2)(A_1 - B_1) + 6B_2 + (a^2 / B^2)(A_2 - B_2)$$

$$D_1^R\begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix} = D\begin{bmatrix} 1 & 1 \\ y & y \end{bmatrix} = 0$$

$$D_1^R\begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix} = -B_1 \exp(-icq_3/4)\left[\exp\left(-iaq_2/\sqrt{3}\right) + 2\cos\left(aq_1/2\right)\exp\left(iaq_2/2\sqrt{3}\right)\right]$$

$$-(a^2/2A^2)(A_1 - B_1)\cos(aq_1/2).\exp\left(iaq_2/2\sqrt{3} - icq_3/4\right)$$

$$D_1^R\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix} = -\left(ia^2/2\sqrt{3A^2}\right)(A_1 - B_1)\exp\left(iaq_2/2\sqrt{3} - icq_3/4\right)\sin\left(aq_1/2\right)$$

$$D_1^R\begin{bmatrix} 1 & 2 \\ x & z \end{bmatrix} = (iac/4A^2)(A_1 - B_1)\exp\left(iaq_2/2\sqrt{3} - icq_3/4\right)\sin\left(aq_1/2\right)$$

$$D_1^R\begin{bmatrix} 1 & 3 \\ x & x \end{bmatrix} = 2B_2 \exp\left(iaq_2/\sqrt{3}\right)\cos\left(cq_3/2\right) - 4\left[B_2 + a^2(A_2 - B_2)/4B^2\right]$$

$$\left[\exp\left(-iaq_2/2\sqrt{3}\right)\cos\left(aq_1/2\right)\cos\left(cq_3/2\right)\right] \qquad (\mathbf{3.9})$$

$$D_1^R\begin{bmatrix} 1 & 3 \\ x & y \end{bmatrix} = (ia^2/\sqrt{3}B^2)(A_2 - B_2)\exp\left(-iaq_2/2\sqrt{3}\right)\cos\left(cq_3/2\right).\mathrm{Sin}\left(aq_1/2\right)$$

$$D_1^R\begin{bmatrix} 1 & 3 \\ x & z \end{bmatrix} = (ac/B2)(A_2 - B_2)\exp\left(-iaq_2/2\sqrt{3}\right)\sin\left(cq_3/2\right).\mathrm{Sin}\left(aq_1/2\right)$$

$$D^{R}_{1}\begin{bmatrix}1&3\\ y&x\end{bmatrix}=D\begin{bmatrix}1&1\\ y&z\end{bmatrix}=0$$

$$D^{R}_{1}\begin{bmatrix}1&2\\ y&y\end{bmatrix}=-\left[B_1+(a^2/3A2)(A_1-B_1)\right]\exp(-iaq_2/\sqrt{3}-icq_3/4)$$

$$-2\left[B_1+(a^2/12A^2)(A_1-B_1\right]\exp(iaq_2/2\sqrt{3}-icq_3/4)\cos(aq_1/2)$$

$$D^{R}_{1}\begin{bmatrix}1&2\\ y&z\end{bmatrix}=-(ac/4\sqrt{3}A^2)(A_1-B_1)\exp(-iaq_2/\sqrt{3}-icq_3/4)$$

$$+(ac/4\sqrt{3}A^2)(A_1-B_1)\exp(iaq_2 2/\sqrt{3}-icq_3).\cos(aq_1/2)$$

$$D^{R}_{1}\begin{bmatrix}1&3\\ y&y\end{bmatrix}=-2\left[B_2+(a^2/3B2)(A_2-B_2)\right]\exp(iaq_2/\sqrt{3})\cos(cq_3/2)$$

$$-4\left[B_2+(a^2/12B^2)(A_2-B_2)\right]\exp(-iaq_2/2\sqrt{3})\cos(aq_1/2)\cos(cq_3/2)$$

$$D^{R}_{1}\begin{bmatrix}1&3\\ y&z\end{bmatrix}=-(-iac/\sqrt{3}B^2)(A_2-B_2)\exp(iaq_2/\sqrt{3})\sin(cq_3/2)$$

$$+(iac/\sqrt{3}B^2)(A_2-B_2)\exp(-iaq/2\sqrt{3}).\sin(cq_3/2).\cos(aq_1/2)$$

$$D^{R}_{1}\begin{bmatrix}1&1\\ z&z\end{bmatrix}=-3A_1+(3c^2/16A^2)(A_1-B_1)+6B_2+(3c^2/2B^2)(A_2-B_2)$$

$$D^{R}_{1}\begin{bmatrix}1&2\\ z&z\end{bmatrix}=-\left[B_1+(c^2/16A^2)(A_1-B_1\right]\left[\exp(-iaq_2/\sqrt{3}-icq_3/4)\right.$$
$$\left.+2\,\mathrm{Cos}(aq_1/2).\exp(iaq_2/2\sqrt{3}-icq_3/4)\ \right]$$

$$D^{R}_{1}\begin{bmatrix}1&3\\ z&z\end{bmatrix}=-\left[B_2+(c^2/4B^2)(A_2-B_2\right]\begin{bmatrix}2\exp(iaq_2/\sqrt{3})\cos(cq_3/2)\\ +4\exp(-iaq_2/2\sqrt{3}).\cos(aq_1/_1/2)\cos cq_3/2)\end{bmatrix}$$

$$D_1^R\begin{bmatrix}2&2\\x&x\end{bmatrix}=D_1\begin{bmatrix}2&2\\y&y\end{bmatrix}=6B_1+\left(a^2/A^2\right)\left(A_1-B_1\right)$$

$$D_1^R\begin{bmatrix}2&2\\x&x\end{bmatrix}=D_1^R\begin{bmatrix}2&2\\y&y\end{bmatrix}=D_1^R\begin{bmatrix}2&2\\y&z\end{bmatrix}=0$$

$$D_1^R\begin{bmatrix}2&3\\x&x\end{bmatrix}=D_1^R\begin{bmatrix}1&2\\x&x\end{bmatrix}$$

$$D_1^R\begin{bmatrix}2&3\\x&y\end{bmatrix}=D_1^R\begin{bmatrix}1&2\\x&y\end{bmatrix}_1=D_1^R\begin{bmatrix}2&3\\x&z\end{bmatrix}=D_1^R\begin{bmatrix}1&2\\X&Z\end{bmatrix}$$

$$D_1^R\begin{bmatrix}2&3\\y&y\end{bmatrix}=D_1^R\begin{bmatrix}1&2\\y&y\end{bmatrix}_1=D_1^R\begin{bmatrix}2&3\\y&z\end{bmatrix}=D_1^R\begin{bmatrix}1&2\\y&Z\end{bmatrix}$$

$$D_1^R\begin{bmatrix}2&2\\z&z\end{bmatrix}=6B_1+\left(3c^2/8A^2\right)\left(A_1-B_1\right)$$

$$D_1^R\begin{bmatrix}2&3\\z&z\end{bmatrix}=D_1^R\begin{bmatrix}1&2\\z&z\end{bmatrix}_1=D_1^R\begin{bmatrix}3&3\\y&y\end{bmatrix}=D_1^R\begin{bmatrix}1&1\\X&x\end{bmatrix}$$

$$D_1^R\begin{bmatrix}3&3\\z&y\end{bmatrix}=D_1^R\begin{bmatrix}3&3\\x&z\end{bmatrix}=D_1^R\begin{bmatrix}3&3\\y&z\end{bmatrix}=0$$

$$D_1^R\begin{bmatrix}3&3\\z&z\end{bmatrix}=D_1^R\begin{bmatrix}1&1\\z&z\end{bmatrix}$$

The rest of the matrix elements are obtained by utilizing Hermitian properties of matrix.

3.3.2 THE THREE-BODY SHORT RANGE MATRIX ELEMENTS:

When De Launay[78] type of angular forces (not invariant to rigid body rotation) are used to calculate the elastic constants by the method of long wavelength limit, the expression for the compressibility is found to contain angular force constants. This result is unrealistic. Since the angles

do not change when a crystal is subjected to uniform compression, it is obvious that the compressibility calculated by means of the static deformation method will not involve angular force constants at all and will result in a different answer. A second method for the calculation of angular forces was proposed by Born[12] in his first treatment of the diamond lattice. He introduced angular forces in a manner which eliminated the effect of rigid body rotation. In his treatment the angular forces arise when there is a change in the angle included between the pair of bonds connecting two neighbors with the central atom. Since this angle is not affected by rigid body rotations, such motions do not give rise to restoring forces.

Based on the idea of Born[12], Clark et al[32] have used angular forces for the treatment of BCC lattice and this model is known as CGW angular force model. In this model, the force is considered to arise from the resistance to the deformation of the angles of the triangles formed by an atom with its two neighbors. To evaluate the changes in the angles of a triangle, a comparison is made between the triangles (formed by these atoms) in the equilibrium position and the project ion of the deformed triangle on to the equilibrium plane. Since the number of such triangles is quite large, the arithmetical labor is tedious. However, the method is quite logical. Therefore, the matrix elements of CdI_2 structure are to be calculated applying CGW type angular forces[32].

To calculate the matrix elements for the CdI_2 structure a triangle ABC is considered with metal atom A lying at the centre of the octahedron and two first nearest chalcogen atoms

$$B(-a/2, a/2\sqrt{3}, a/4) \text{ and } C(0, a/\sqrt{3}, a/4)$$

lying in the upper layer. Total three such type of triangles are formed. Three such types of triangles are again formed when metal atom A is at the origin and two first nearest chalcogen atoms are in the lower layer (Figure **1.3a**). All these triangles are isosceles. If K_1 and K_2 are the force constants associated with the angles B (or C) and at A in the triangle ABC, then the matrix elements can be calculated. The matrix elements are as follows.

$$D_2^R\begin{bmatrix}1&1\\x&x\end{bmatrix}=18a^4\sigma_1/X+(1/X)(12a^4+9a^2c^2/2+27c^4/16)\sigma_2$$

$$D_2^R\begin{bmatrix}1&1\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}1&1\\x&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}1&2\\x&z\end{bmatrix}=-(3a^2/2x)(4a^2+3c^2/4)(2\sigma_1+\sigma_2)\exp(-iE_1)$$

$$-(C_1/2x)\left[6a^2(2a^2+3c^2/4)\sigma_1+(12a^4+27a^2c^2/4+27c^4/8)\sigma_2\right]\exp(-iE_2)$$

$$D_2^R\begin{bmatrix}1&2\\x&y\end{bmatrix}=(i\sqrt{3}S_1/2x)\left[6a^2(2a^2+3c^2/4)\sigma_1-(4a^4+3a^2c^2/4+9c^4/8)\sigma_2\right]$$

.exp (-iE_2)

$$D_2^R\begin{bmatrix}1&2\\x&z\end{bmatrix}=(icS_1/2a)D_2^R\begin{bmatrix}1&1\\x&x\end{bmatrix}\exp(-iE_2)$$

$$D_2^R\begin{bmatrix}1&3\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}1&3\\x&y\end{bmatrix}=D_2^R\begin{bmatrix}1&3\\x&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}1&1\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}1&1\\x&y\end{bmatrix},D_2^R\begin{bmatrix}1&1\\y&y\end{bmatrix}=D_2^R\begin{bmatrix}1&1\\x&x\end{bmatrix},D_2^R\begin{bmatrix}1&1\\y&z\end{bmatrix}=0 \qquad \textbf{(3.10)}$$

$$D_2^R\begin{bmatrix}1&2\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&y\end{bmatrix}$$

$$D_2^R\begin{bmatrix}1&2\\y&y\end{bmatrix}=\left[9a^2c^2\sigma_1-(4a^2+15a^2c^2/4+9c^4/4)2\sigma_2\right]\left[\exp(-iE_1\right]/4x$$

$$-C_1\left[18a^2(2a^2+c^2/4)\sigma_1+(20a^4+21a^2c^2/4+9c^4/8)\sigma_2\right]\left[\exp(iE_2)\right]/2x$$

$$D_2^R\begin{bmatrix}1&2\\y&z\end{bmatrix}=-\sqrt{3}c\left[3a^2\sigma_1+(2a^3+3ac^2/4+9c^4/32a)\sigma_2\right]\left[\exp(-iE_1)\right.$$
$$\left.-C_1\exp(-iE_2)\right]/X$$

$$D_2^R\begin{bmatrix}1&3\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}1&3\\y&y\end{bmatrix}=D_2^R\begin{bmatrix}1&3\\y&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}1&1\\z&x\end{bmatrix}=D_2^R\begin{bmatrix}1&1\\z&y\end{bmatrix}=0\,D_2^R\begin{bmatrix}1&1\\z&z\end{bmatrix}=\left[27a^2c^2/2x\right][2\sigma_1+\sigma_2]$$

$$D_2^R\begin{bmatrix}1&2\\z&x\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&z\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}1&2\\z&y\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\y&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}1&2\\z&z\end{bmatrix}=-(9a^2c^2/2x)\,[2\sigma_1+2\sigma_2]\,\left[\exp(-iE_1)+2C_1(\exp(-iE_2)\right]$$

$$D_2^R\begin{bmatrix}1&3\\z&x\end{bmatrix}=D_2^R\begin{bmatrix}1&3\\z&y\end{bmatrix}=D_2^R\begin{bmatrix}1&3\\z&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}2&1\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&x\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}2&1\\x&y\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&y\end{bmatrix},\ D_2^R\begin{bmatrix}2&1\\x&z\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}2&2\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}1&1\\x&x\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}2&2\\x&y\end{bmatrix}=D_2^R\begin{bmatrix}2&2\\x&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}2&3\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&x\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}2&3\\x&y\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&y\end{bmatrix},\ D_2^R\begin{bmatrix}2&3\\x&z\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\x&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}2&1\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}2&1\\x&y\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}2&1\\y&y\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\y&y\end{bmatrix},\ D_2^R\begin{bmatrix}2&1\\y&z\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\y&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}2&2\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}2&2\\y&z\end{bmatrix}=0\ ,\ D_2^R\begin{bmatrix}2&2\\y&y\end{bmatrix}=D_2^R\begin{bmatrix}2&2\\x&x\end{bmatrix}$$

$$D_2^R\begin{bmatrix}2&3\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}23\\XY\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}23\\YY\end{bmatrix}=D_2^R\begin{bmatrix}12\\YY\end{bmatrix},\ D_2^R\begin{bmatrix}23\\YZ\end{bmatrix}=D_2^R\begin{bmatrix}12\\YZ\end{bmatrix}$$

$$D_2^R\begin{bmatrix}2&1\\z&x\end{bmatrix}=D_2^R\begin{bmatrix}2&1\\x&z\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}2&1\\z&y\end{bmatrix}=D_2^R\begin{bmatrix}2&1\\y&z\end{bmatrix},\ D_2^R\begin{bmatrix}2&1\\z&z\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\z&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}2&2\\z&x\end{bmatrix}=D_2^R\begin{bmatrix}2&2\\z&y\end{bmatrix}=0\ ,\ D_2^R\begin{bmatrix}2&2\\z&z\end{bmatrix}=2\ D_2^R\begin{bmatrix}1&1\\z&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}2&3\\z&x\end{bmatrix}=D_2^R\begin{bmatrix}2&3\\x&z\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}2&3\\z&y\end{bmatrix}=D_2^R\begin{bmatrix}2&3\\y&z\end{bmatrix},\ D_2^R\begin{bmatrix}2&3\\z&z\end{bmatrix}=D_2^R\begin{bmatrix}1&2\\z&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}3&1\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}3&1\\x&y\end{bmatrix}=\ D_2^R\begin{bmatrix}3&1\\x&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}3&2\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}2&3\\x&x\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}3&2\\x&y\end{bmatrix}=D_2^R\begin{bmatrix}2&3\\x&y\end{bmatrix},D_2^R\begin{bmatrix}3&2\\x&z\end{bmatrix}=D_2^R\begin{bmatrix}2&3\\x&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}3&3\\x&x\end{bmatrix}=D_2^R\begin{bmatrix}1&1\\x&x\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}3&3\\x&y\end{bmatrix}=D_2^R\begin{bmatrix}3&3\\x&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}3&1\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}3&1\\y&y\end{bmatrix}=D_2^R\begin{bmatrix}3&1\\y&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}3&2\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}3&2\\x&y\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}3&2\\y&y\end{bmatrix}=D_2^R\begin{bmatrix}2&3\\y&y\end{bmatrix},D_2^R\begin{bmatrix}3&2\\y&z\end{bmatrix}=D_2^R\begin{bmatrix}2&3\\y&z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}3&3\\y&x\end{bmatrix}=D_2^R\begin{bmatrix}3&3\\y&z\end{bmatrix}=0\ ,\ D_2^R\begin{bmatrix}3&3\\y&y\end{bmatrix}=D_2^R\begin{bmatrix}1&1\\y&y\end{bmatrix}$$

$$D_2^R\begin{bmatrix}3&1\\z&x\end{bmatrix}=D_2^R\begin{bmatrix}3&1\\z&y\end{bmatrix}=D_2^R\begin{bmatrix}3&1\\z&z\end{bmatrix}=0$$

$$D_2^R\begin{bmatrix}3 & 2\\ z & x\end{bmatrix}=D_2^R\begin{bmatrix}3 & 2\\ x & z\end{bmatrix}\ ,\ D_2^R\begin{bmatrix}3 & 2\\ z & y\end{bmatrix}=D_2^R\begin{bmatrix}3 & 2\\ y & z\end{bmatrix}\ ,D_2^R\begin{bmatrix}3 & 2\\ z & z\end{bmatrix}=D_2^R\begin{bmatrix}2 & 3\\ z & z\end{bmatrix}$$

$$D_2^R\begin{bmatrix}3 & 3\\ z & x\end{bmatrix}=D_2^R\begin{bmatrix}3 & 3\\ z & y\end{bmatrix}=0\ ,\ D_2^R\begin{bmatrix}3 & 3\\ z & z\end{bmatrix}=D_2^R\begin{bmatrix}1 & 1\\ z & z\end{bmatrix}$$

Where

$C_1 = \text{Cos}(aq_1/2)$, $S_1 = \text{Sin}(aq_1/2)$

$$E_1 = (aq_1/\sqrt{3}) + (cq_3/4),\ E_2 = (-aq_1/2\sqrt{3}) + (cq_3/4)$$

$$\sigma_1 = (a^2/3 + c^2/16)K_1, \qquad \sigma_2 = (a^2/3 + c^2/16)K_2,$$

$$x = (a^2/3 + c^2/16)\ (4a^2 + 3c^2/4)\ (a^2 + 3c^2/4)$$

3.3.3 THE COLUMBIC INTERACTION

As CdI_2 structure is a very complex layered structure, we did not consider the long range Coulomb interaction in this case i.e. we have taken the third term of equation [**3.l]** as zero.

3.4

EVALUTION OF THE FORCE CONSTANTS

To calculate the lattice dynamical properties of the materials in different structures, the knowledge of force constants involved in the secular determinant is essential. These force constants can be calculated from the experimental values of various elastic constants and the phonon frequencies at specified wave vectors. In general any crystalline material is associated with 81 elastic constants, though all of these are not independent of one another. It has been found that a cubic lattice possesses only three independent elastic constants, namely, C_{11}, C_{12} and C_{44}, whereas a crystal with CdI_2 structure is associated with six independent elastic constants C_{11}, C_{12} and C_{13}, C_{15}, C_{33} and C_{44}. These elastic constants are related to various force constants in the long wavelength limit. This is done by making use of a physically plausible assumption that for $q \rightarrow 0$ (long wavelength limit), one may disagreed the atomic nature and treat the solid as a continues medium and hence the linear relation $w=v_s q$ (v_s is the velocity of sound) holds good because the interatomic spacing of atoms in solid becomes much smaller than use wavelength. That is at long wavelength limit; the elastic waves do not see the discreetness of the lattice and propagates as if through a continuum. Thus a correspondence can be established between elastic and lattice wave in long wave length limit.

In the present work, the long wave length limit is used to establish the relation between elastic constants and force constants of the fluorite and CdI_2 structures. For the fluorite structure the five unknown force constant parameter A_1, A_2, A_3, B_1, B_2, K_1 and K_2 are calculated by using three elastic constants and two zone centre frequencies. The lattice equilibrium condition is also used. Whereas the four force constants A_1, A_2

K_1, K_2 are calculated by making use of four experimental zone centre frequencies. The expression for elastic constant of CdI_2 structure is not derived here because of complications in the results. The equation thus obtained model are given below.

3.4.1 THE FLUORITE STRUCTURE

$$2aC_{11} = 4/3(A_1 + 2B_2) + 4(A_2 + 3B_3) + 4(3\sigma_1 + 2\sigma_2) + 3.052(Z^2e^2/V\varepsilon_\infty)$$

$$2aC_{12} = 4/3(A_1 - 4B_1) - 2(2A_2 - 3A_3) - 2(3\sigma_1 + 2\sigma_2) - 5.4046(Z^2e^2/V\varepsilon_\infty)$$

$$2aC_{44} = 4/3(A_1 + 2B_1) + 2(A_2 + 3A_3) + 2(\sigma_1 + 2\sigma_2) + 1.5256(Z^2e^2/V\varepsilon_\infty)$$

$$-\frac{\left[\frac{4}{3}(A_1 - B_1) - 4\sigma_1 - 5.02884(Z^2e^2/V\varepsilon_\infty)\right]^2}{4/3(A_1 + 2B_1) + 4(A_2 + 2B_2) + 8\sigma_1 + 8\sigma_2}$$

$$4/3(A_1 + 2B_1) + 8\sigma_1 + 8\sigma_2 + 4.19(Z^2e^2/Va\varepsilon_\infty) = \{mM/(2m+M)\}\omega^2_{LO}$$

$$4/3\alpha + 8\sigma_1 + 8\sigma_2 + 2.095(Z^2e^2/Va\varepsilon_\infty) = \{mM/(2m+M)\}\omega^2_{LO}$$

$$4/3(A_1 + 2B_1) + 4(A_2 + B_2) + 8\sigma_1 + 8\sigma_2) = m\omega^2_R \qquad \textbf{(3.11)}$$

Where $\sigma_1 = 16/9K_1 and \sigma_2 = 12/9K_2$

Assuming K_3=K_4= o and A_3=A_4,B_3=B_4=o

Here, Ze is the charge on the cation and – Ze/2 on the fluorine ion. V (=a^3/4) is the volume of the unit cell and ε_∞ being the high frequency dielectric constant. the effective charge $Z_{eff}\left(Z_{eff} = Z^2/\varepsilon\infty\right)$ is evaluated with the help of LST relation[78] given by

$$Z^2_{eff} = \frac{\mu V(\omega^2_{1.O} - \omega^2_{TO}}{2\pi e^2} \qquad \textbf{(3.12)}$$

Where μ is the reduced mass ($1/\mu$ =1/m+ 2/M), m being mass of fluorine ion and M that of cation ω_{LO}, ω_{TO} and ω_R represents the optical and Raman frequency respectively at the zone-centre.

3.4.2 THE Cdl_2 STRUCTURE

$$3B_1 + \left(3c^2/16A^2\right)\left(A_1 - B_1\right) + \left(3c^2/B^2\right)A_2 + \left(27a^2c^2/x\right)\sigma_1 + \left(27a^2c^2/2x\right)\sigma_2 = m\omega^2{}_{A1g}$$

$$3B_1 + \left(a^2/2A^2\right)\left(A_1 - B_1\right) + \left(2a^2/B^2\right)A_2 + \left(18a^4/x\right)\sigma_1 + \left(12a^4 + 9a^2c^2/2 + 27c^4/16\right)/x\sigma_2 = m\omega^2{}_{Eg}$$

$$3B_1 + \left(3c^2/16A^2\right)\left(A_1 - B_1\right) + \left(27a^2c^2/x\right)\sigma_1 + \left(27a^2c^2/2x\right)\sigma_2 = \{mM/(2m+M)\}\omega^2{}_{A2u}$$

$$3B_1 + \left(a^2/2A^2\right)\left(A_1 - B_1\right) + \left(18a^4/x\right)\sigma_1 + \left(12a^4 + 9a^2c^2/2 + 27c^2/16\right)/x]\sigma_2 = \{mM/(2m+M)\}\omega^2{}_{Eu}$$

(3.13)

Here m and M are the masses of chalcogen and metal atoms respectively and $\omega_{A1g}, \omega_{Eg}, \omega_{A2u}$ and ω_{Eu} being the zone centre frequencies.

3.5

THE LATTICE EQUILIBRIUM CONDITION

The total potential energy per unit – cell of the lattice in the framework of our BBRIM can be expressed as

$$\phi_0 = \frac{1}{2}\alpha_M Z_1 Z_2 \frac{e^2}{r} + 8\phi_1^R\left(r^1\right) + 6\phi_3^R\left(r^n\right) + \phi^B(\delta\theta) \qquad \textbf{(3.14)}$$

Where the madelung constant $\alpha_M = 5.818$ is in terms of two similar atom separations $r^1 = \sqrt{3}/2r,\ r^n = \sqrt{2r}.$ at the equilibrium separation, we use the following condition $\left.\frac{d\phi_0}{dr}\right|_0 = 0$

Where $|_0$ stands for the derivatives to be taken in the equilibrium configuration $\phi_1^R(i = 1,2,3)$ represents the short – range repulsive interaction potential ϕ^R giving rise to the bond bending forces. Numbers before ϕ_1^R describe the number of atoms for first, second and third nearest neighbors. We have finally neglected the force parameter B_4 for fourth neighbor because for all the fluorite structure materials, it is negligibly small. For the fluorite structure, therefore. The above condition gives.

$$B_1 + B_2 + B_3 - 1/6\alpha_M Z_1 Z_2 = 0 \qquad \textbf{(3.15)}$$

Where B_k (k=1, 2, 3) are force constants as defined earlier i.e.

$$B_k = \frac{1}{r}\left(\frac{d\phi_1^R}{dr}\right)_{r=r_k}$$

In the case of CdI_2 structure, however, equation **(3.15)** gives

$$B_1 - 1/6a_M Z_1 Z_2 = 0 \qquad \textbf{(3.16)}$$

$$A = \sqrt{\left(a^2/3 + c^2/16\right)}$$

$$B = \sqrt{\left(a^2/3 + c^2/4\right)}$$

Here '**a**' and '**c**' are the lattice constants.