Chapter 3

General Theory of Lattice Vibrations and Present Theoretical Models

3.1 Introduction

The study of phonon assisted vibrational properties is of fundamental significance in the theory of solid state physics. This is primarily because the interatomic interactions and types of chemical bonding govern number of physical properties of solids. Such as thermal and electrical conductivities, specific heat, Elastic, optic and dielectric constant etc. These properties depend on the dynamics of the atoms (or ions) in crystal and hence their study requires detailed information about the actual form of phonon frequency spectrum. This fact has led to the development of the various lattice dynamical theories, which in turn predict useful feature of materials required for the development of modern technology. Such theories are extremely important to understand phonon properties and structural phase transition in different class of solid state materials.

The dynamical properties of solid mentioned above can be qualitatively explained by using the concept that the atoms, which constitute the solid, are bound together by harmonic forces, generally termed as "Harmonic approximations". The theoretical framework originally proposed by Born and Von Karman [1] considers the crystals as perfect infinite assembly of atoms connected through harmonic force constants, free from any external stress, and that the dynamics of the solid can be solving their equations of motion. However since then, the field of phonon physics has witnessed wide and diversified developments starting from semi microscopic models to *ab –intio* theories, most of them having different ideas and physical significance and is important in their right. Some of these model theories which are common for any class of solids (ionic, insulating, semiconducting and superconducting etc.) are the rigid ion model (RIM) [2], Shell Model (SM) [3,4,5], deformation dipole model (DDM) [6], Breathing shell model (BSM) [7], double shell model [8], force constant model [9-11] and several others [12-13] which includes additional interactions or effects in the framework of the above theories. Several reviews are available in literature for ionic and semiconducting materials [14-18],which discuss the upto date development of model theories, their success in predicting properties of materials and future scopes in this direction. In addition to the model theories, several semi empirical and microscopic theories have been formulated and largely exploited for the semiconductors [19]. Such *ab-intio* theories however are found not to predict accurate description of the dynamics and structural properties of the solids at high pressure because of the approximations involved in solving the many body problems [20]. We will only refer to the literature, for such theoretical development without going into much detail.

In the present theoretical analysis, we have used two model theories namely rigid ion and deformation bond approximation model to describe the lattice vibrations in considered compound semiconductors having zinc blende structure. Therefore, we only describe the theories. However some other models relevant to the zinc blende semiconductors are also briefly described. In the following, we begin with the most general theory of lattice vibrations in solids, followed by their extensions to the ionic crystals and semiconducting compounds.

3.2 General theory of lattice vibrations

The general theory of lattice vibrations considers the solid to be comprised of discrete infinite atomic chains and was first proposed by Born and Von Karman [1]. The development of such a theory is based on new approximations as outlined below.

3.2.1 The Cyclic boundary Condition

The propagations of phonons through a lattice can be considered by imposing suitable boundary conditions on the components of the displacement vectors of the constituting atoms. This can be achieved by proper normalizations of the number of models and ignoring the surface effects. In this approximation, one divides an infinite crystal into several macro crystals each of which contains N (= L x L x L) unit cells, where L is the dimensions of the side of the macro crystal. It is assumed that the equivalents atoms on the opposite faces move in phase i.e. the atomic displacements are periodic with the dimensions of the macro crystals such that $\vec{u}(lk)=\vec{u}(l+1,k)$.

The cyclic boundary conditions therefore requires that,

$$e^{i\vec{q}.L\vec{a_1}}=e^{i\vec{q}.L\vec{a_2}}=e^{i\vec{q}.L\vec{a_3}}=1 \qquad (1)$$

Where $\vec{q}$ is the phonon propagations and $\vec{a_i}=(i=1,2,3)$ are the lattice translational vectors respectively. Thus the cyclic boundary conditions allows a uniform distributions of the possible

Wave vectors in the Brillouin zone (BZ) of the lattice.

3.2.2 The Adiabatic Approximation

The adiabatic approximation allows the separations of the low energy lattice vibrations and the high energy electronic excitation from each other. In other words, it can be said that it separates the electronic and the nuclear motions in the solids. Since the mass of the nuclei is very large as compared to that of the electrons, therefore the nuclei can be considered to be practically at rest. Thus, this approximation allows the electrons to follow any displacement of the cores instantaneously by taking up a force free equilibrium configurations and hence the electronic coordinates can be eliminated.

3.2.2 I General Notations

The position vector of the lth atom in the Kth unit cell in equilibrium is given by [1]

$$\vec{X}(l\,k)=\vec{X}(l)+\vec{X}(k) \qquad (2)$$

Where,

$$\vec{X}(l)=l_1\vec{a}1+l_2\vec{a}2+l_3\vec{a}3 \qquad (3)$$

With l_1, l_2 and l_3 as the integers, called cell indices and $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$, as the basis vectors of the crystal lattice. The volume of a unit cell of a direct lattice is given as

$$V=\overline{a_1}\cdot\left(\overline{a_2}\times\overline{a_3}\right) \tag{4}$$

The vector distance between two ions (lk) and (l'k') will be given by

$$\vec{r}\left(lk,l'k'\right)=\vec{r}\left(l'k'\right)-\vec{r}\left(lk\right) \tag{5}$$

In terms of Cartesian components, the position vectors will be represented by

$$X_{\alpha}\left(lk,l'k'\right)=X_{\alpha}\left(l'k'\right)-X_{\alpha}\left(lk\right) \tag{6}$$

3.2.2 II The Hamiltonian in the Harmonic Approximation

The atoms in a crystal vibrate around their equilibrium position. The instantaneous position of the atom (lk) is given by

$$\vec{r}\left(lk\right)=\vec{X}\left(lk\right)+\vec{u}\left(lk\right) \tag{7}$$

Where $\vec{u}$ is a small displacement. The kinetic energy of the lattice can be written as

$$T=\frac{1}{2}\sum_{lk\alpha} m_k\, \dot{u}_{\alpha}^{2}\left(lk\right) \tag{8}$$

With m_k as the mass of the k_{th} atom and $u_{\alpha k}$ as the Cartesian component of $\dot{u}_{\alpha}\left(lk\right)$.

The potential energy being the function of instantaneous position vector, can be written as

$$\Phi=\sum_{lk}\Phi\left(\vec{r}\left(lk\right)\right)=\sum_{lk}\Phi\left(\vec{X}\left(lk\right)+\vec{u}\left(lk\right)\right) \tag{9}$$

For small displacements, the effective potential Φ can be expanded in terms of Taylor's series in powers of $u_\alpha(lk)$ as,

$$\Phi = \Phi(X_\alpha(lk)) + \sum_{lk\alpha} \Phi_\alpha(lk) u_\alpha(lk) + \frac{1}{2}\sum_{lk\alpha}\sum_{lk\beta} \Phi_{\alpha\beta}(lk,l'k') u_\alpha(lk) u_\beta(l'k')$$

$$+\frac{1}{6}\sum_{lk\alpha}\sum_{l'k'\beta}\sum_{l''k''\gamma} \Phi_{\alpha\beta\gamma}(lk,l'k',l''k'') u_\alpha(lk) u_\beta(l'k') u_\gamma(l''k'') + \ldots$$

$$= \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \cdots \qquad (10)$$

Here Φ_0 is the static (or equilibrium) potential energy of the crystal. Φ_1 denotes the potential energy which is linear in displacement and vanishes in equilibrium when there is no net force on the atom and can be expressed as

$$\Phi_\alpha(lk) = \left[\frac{\partial \Phi}{\partial u_\alpha(lk)}\right]_0 = -[F_\alpha(lk)]_0 \qquad (11)$$

In equilibrium, the coefficient $\Phi_\alpha(lk)$ represents the negative of the force acting on the atom at X (lk) along α- direction. The symbol 'o' within the parenthesis signifies the equilibrium value. Φ_2 in equation (10) is quadratic in displacement and depends on the second derivative of the potential energy with respect to atomic displacement, such that,

$$\Phi_{\alpha\beta}(lk,l'k') = \left[\frac{\partial^2 \Phi}{\partial u_\alpha(lk)\partial u_\beta(l'k')}\right]_0 \qquad (12)$$

These coefficients are often called as the force constants and satisfy the following conditions:

(i) The force constants satisfy the symmetry conditions, i.e.

$$\Phi_{\alpha\beta}(lk,l'k') = \Phi_{\beta\alpha}(l'k',lk) \quad \text{and}$$

(ii) $\Phi_{\alpha\beta}(lk,l'k')$ depends only on the vector difference $\left(\bar{x}(l)-\bar{x}(l')\right)$ and not on the individual values and mostly they are denoted by $\Phi_{\alpha\beta}(l'-l,kk')$.

The terms beyond the third, one in equation (10) represents the anharmonic contributions to the crystal potential energy and they are generally neglected in the description of lattice dynamics. This restriction is said to be the harmonic approximation. In the harmonic approximation, therefore Hamiltonian is written as

$$H=\Phi_0+\frac{1}{2}\sum_{lk\alpha} m_k \dot{u}_\alpha^{2}\left(lk\right)+\frac{1}{2}\sum_{lk\alpha}\sum_{lk\beta}\Phi_{\alpha\beta}\left(lk,l'k'\right)u_\alpha\left(lk\right)u_\beta\left(l'k'\right) \tag{13}$$

The expression can be directly used to derive the equation of motion and dynamical matrix as outlined below.

3.2.2 III The Dynamical Matrix

The equation of motion of the atoms in the lattice can be written from equation (13) as

$$m_k \ddot{u}_\alpha(lk)=-\sum_{l'k'\beta}\Phi_{\alpha\beta}(lk,l'k')u_\beta(l'k') \tag{14}$$

This equation of motion represents an infinite set of simultaneous linear differential equations. The solutions can be sought in the form of plane wave,

$$\bar{u}(lk)=U\left(\frac{k}{q}\right)\exp(i(\bar{q}.\bar{r}(lk)-\omega(\bar{q})t)) \tag{15}$$

Here, $U\left(\frac{k}{q}\right)$ represents the amplitude and is independent of l. $\bar{q}$ is the wave vector and $\omega(\bar{q})$ is the angular frequency associated with wave. Substitution of equation (15) in (14) results in to a set of homogeneous linear equations

$$\omega^2(\vec{q})u_\alpha\begin{pmatrix} k \\ \overline{\vec{q}} \end{pmatrix} = \sum_{k'\beta} D_{\alpha\beta}\begin{pmatrix} kk' \\ \overline{\vec{q}} \end{pmatrix} u_\beta\begin{pmatrix} k' \\ \overline{\vec{q}} \end{pmatrix} \tag{16}$$

For each value of $\vec{q}$. Here $D\begin{pmatrix} kk' \\ \overline{\vec{q}} \end{pmatrix}$ is called the dynamical matrix of order (3n x 3n) whose elements are given by

$$D\begin{pmatrix} kk' \\ \overline{\vec{q}} \end{pmatrix} = (m_k m_{k'})^{-\frac{1}{2}} \sum_{l'} \Phi_{\alpha\beta}(l'-1, kk')\, e^{-i\bar{q}\bar{r}(lk,l'k')} \tag{17}$$

The equation (17) can be written in matrix notation as

$$\omega^2(\vec{q})U(\vec{q}) = D(\vec{q})U(\vec{q}) \tag{18}$$

The condition for the non-trivial solution for the wave amplitude of 18 leads to the following characteristics equation

$$\left| \mathbf{D}(\vec{q}) - \omega^2(\vec{q})\, m\ \mathbf{I} \right| = 0 \tag{19}$$

Where I is the unit matrix of order 3n and m is a (3n x 3n) diagonal matrix defined as

$$m_{\alpha\beta}(kk') = m_k \delta_{\alpha\beta} \delta_{kk'} \tag{20}$$

The characteristics equation 19 is a (3n x 3n) determinant and it's solution yields 3n values of $\omega_j^2(\vec{q})$ .The relation given by,

$$\omega = \omega_j(\vec{q}), \quad j = 1,2,3.....n \tag{21}$$

is called the dispersion relation. It is found that out of 3n solutions for each wave vector $\vec{q}$, three frequencies go to zero as $\vec{q}$ tends to zero. Such modes are called acoustics mode. The remaining 3(n-1) branches tend to finite frequencies as $\vec{q}$ approaches to zero. Such modes in binary crystals are found to interact strongly with photon and hence are called optic modes. However the choice of $\vec{q}$ is restricted by the cyclic boundary condition of the crystal, given by

$$\vec{q} = \frac{h_1\vec{b}1 + h_2\vec{b}2 + h_3\vec{b}3}{N} \tag{22}$$

here h_1, h_2 and h_3 are integer triplets and N is the number of unit cells. $\vec{b}_i$ (i=1,2,3) are the reciprocal lattice vectors. In terms of the Eigen vectors $\vec{e}\left(\frac{k}{\vec{q}}, j\right)$, the equation 16 can alternatively be written as,

$$\omega_j^2(\vec{q})\, e_\alpha\left(\frac{k}{\vec{q}}, j\right) = \sum_{k\beta} D_{\alpha\beta}\left(\frac{k}{\vec{q}}\right) e_\beta\left(\frac{k}{\vec{q}}, j\right) \tag{23}$$

The Eigen vector $\vec{e}\left(\frac{k}{\vec{q}}, j\right)$ satisfy the orthonormality and closure conditions

$$\sum_{k\alpha} \overset{*}{e_\alpha}\left(\frac{k}{\vec{q}}, j\right) e_\alpha\left(\frac{k}{\vec{q}}, j\right) = \delta_{jj} \tag{24}$$

$$\sum_{j} \overset{*}{e_\beta}\left(\frac{k}{\vec{q}}, j\right) e_\alpha\left(\frac{k}{\vec{q}}, j\right) = \delta_{\alpha\beta}\delta_{kk'} \tag{25}$$

Thus the lattice dynamical problems revolve around the determination of the eigen values $(\omega(\vec{q}))$ and eigen vectors $\vec{e}\left(\frac{k}{\vec{q}}, j\right)$, corresponding to the dynamical matrix $D(\vec{q})$.

3.3 Present Model Theories

The physical properties of solids depends upon the constituent atoms (or ions) of the crystals and hence their study requires the knowledge of actual form of phonon frequency spectrum which can be achieved by means of theoretical models of lattice dynamics. Inspired by well known Einstein model of independent atomic oscillators [21, 22], Debye [23] and Born and

Von Karman [24] developed more meaningful models for coupled oscillators. While Debye theory considers the solid to be continuous that of BvK theory deals with a lattice and provides the foundation of modern theory. On account of its continuous background, the Debye model ignored dispersion, polarization, and anisotropy of the waves in the lattice. It also provided for an artificial cutoff frequency. The Debye theory held the field completely and eclipsed the BvK theory for about twenty five years till 1935, when the later was reviewed by Blackman [25-29] who showed qualitatively that the BvK theory provided complete answer to the deficiencies of the Debye theory. Blackman's work gradually led to the development of the modern lattice theory.

3.3.1 Rigid Ion Model

In order to define the notations, we recall the basic formula from ref. [30]. We follow as closely as possible the conventions used by Maradudin et al. [31]. The zinc blende lattice is defined by the elementary translations

$$a_1 = \frac{a}{2}(0,1,1), \tag{26}$$

$$a_2 = \frac{a}{2}(1,0,1), \tag{27}$$

$$a_3 = \frac{a}{2}(1,1,0), \tag{28}$$

and basis vectors $x(k=1)=0, \quad x(k=2)=\frac{a}{4}(1,1,1).$ (29)

Here a stands for lattice spacing and the unit cell volume is $v_a = \frac{a^3}{4}$.

Cation occupies the sites with k = 1, anion the sites with k = 2. The short range interactions $\Phi_{\alpha\beta} = (lk, l'k')$ [31].

$$\Phi(1,2)=\begin{bmatrix} A & B & B \\ B & A & B \\ B & B & A \end{bmatrix}, \tag{30}$$

$$\Phi(1,1')=\begin{bmatrix} C_1 & D_1 & E_1 \\ D_1 & C_1 & E_1 \\ -E_1 & -E_1 & F_1 \end{bmatrix}, \tag{31}$$

$$\Phi(2,2')=\begin{bmatrix} C_2 & D_2 & -E_2 \\ D_2 & C_2 & -E_2 \\ E_2 & E_2 & F_2 \end{bmatrix}, \tag{32}$$

Zn and S are the sites.

$$x(Zn') \equiv x(\frac{a}{2}(1,1,0),1) = 0; \quad x(S) \equiv x(0,2) = \frac{a}{4}(1,1,1) \tag{33}$$

Zn' and S' are abbreviations for the lattice sites.

$$x(Zn') \equiv x(\frac{a}{2}(1,1,0),1) = \frac{a}{2}(1,1,1) \tag{34}$$

$$x(S') \equiv x(\frac{a}{2}(1,1,0),2) = \frac{a}{4}(3,3,1) \tag{35}$$

(Second neighbors). This implies that the "C-type" dynamical matrix [31].

$$C^{sr}_{\alpha\beta}\left(\frac{kk'}{K}\right) \equiv \frac{1}{\sqrt{M_k M_{k'}}} \sum_{l-l'} \Phi_{\alpha\beta}(lk,l'k')\exp\{ik(x(l'k')-x(lk))\} \tag{36}$$

M_l is the mass of the atom k and K is the wave vector.

The choice of the phase factor in all the k-space matrices used in this work is the same as in equation (36).

The static ionic charge on cation is

$$e_{\alpha\beta}(k=1)=Z_1\delta_{\alpha\beta} \tag{37}$$

And the opposite on anion, k=2. The deformabilities are

$$m(1,2)=\frac{1}{3}\begin{bmatrix} -\gamma_1 & -\gamma_3 & -\gamma_3 \\ -\gamma_3 & -\gamma_1 & -\gamma_3 \\ -\gamma_3 & -\gamma_3 & -\gamma_1 \end{bmatrix}, \tag{38}$$

Short range part of the dynamical matrix defined by equation (36) with the force parameters,

$$C^{sr}_{\alpha\alpha}\left(\frac{kk'}{K}\right)=-4M_k^{-1}\left\{A+C_k(2-C_{2\alpha}(C_{2\beta}+C_{2\gamma}))+F_k(1-C_{2\beta}C_{2\gamma})\right\} \tag{39}$$

$$C^{sr}_{\alpha\beta}\left(\frac{kk'}{K}\right)=-4M_k^{-1}\left\{D_kS_{2\alpha}\,S_{2\beta}+(-1)^k iE_kS_{2\gamma}(C_{2\alpha}-C_{2\beta})\right\} \tag{40}$$

$$C^{sr}_{\alpha\alpha}\left(1,\frac{2}{K}\right)=+4(M_1M_2)^{-\frac{1}{2}}A(C_\alpha C_\beta C_\gamma-iS_\alpha S_\beta S_\gamma) \tag{41}$$

$$C^{sr}_{\alpha\beta}\left(1,\frac{2}{K}\right)=\div 4(M_1M_2)^{-\frac{1}{2}}B(-S_\alpha S_\beta C_\gamma+iC_\alpha C_\beta S_\gamma) \tag{42}$$

$$C_\alpha\equiv\cos\left(\frac{ak_\alpha}{4}\right);\quad C_{2\alpha}\equiv\cos\left(\frac{ak_\alpha}{2}\right);\quad S_\alpha\equiv\sin\left(\frac{ak_\alpha}{4}\right);\ S_{2\alpha}\equiv\sin\left(\frac{ak_\alpha}{2}\right); \tag{43}$$

$$k=1,2;\{\alpha,\beta,\gamma\}=\{1,2,3\} \tag{44}$$

$$m(2;1)=\frac{1}{3}\begin{bmatrix} +\gamma_2 & +\gamma_4 & +\gamma_4 \\ +\gamma_4 & +\gamma_2 & +\gamma_4 \\ +\gamma_4 & +\gamma_4 & +\gamma_2 \end{bmatrix}, \tag{45}$$

The local electric polariziabilities

$$a(1;1)=\begin{bmatrix} \alpha 2 & 0 & 0 \\ 0 & \alpha 2 & 0 \\ 0 & 0 & \alpha 2 \end{bmatrix}, \tag{46}$$

And the non local ones

$$a(1;2)=\begin{bmatrix} \alpha 3 & \alpha 4 & \alpha 4 \\ \alpha 4 & \alpha 3 & \alpha 4 \\ \alpha 4 & \alpha 4 & \alpha 3 \end{bmatrix}, \tag{47}$$

With equation 37 – 47 the dipole induced at the site (lk) reads

$$p_{\alpha}(lk)=\sum_{\beta} e_{\alpha\beta}(k)u_{\beta}(lk)+\sum_{l'k'\beta} m_{\alpha\beta}(lk';l'k')u_{\beta}(l'k')+\sum_{l'k'\beta} a_{\alpha\beta}(lk';l'k')E_{\beta}^{eff}(l'k'), \tag{48}$$

Where $E^{eff}(lk)$ is the effective field on the site (lk).

The matrix **m** with blocks m (lk, l'k') is not symmetric in $(lk)\leftrightarrow(l'k')$ but its blocks satisfy the condition of translational invariance [31]. The matrix **a** with blocks a (lk, l'k') is symmetric but does not obey the translational invariance. The Fourier transform N(k) and a(k) of these two matrices are defined by the equation analogous to equation (36)

$$N_{\alpha\beta}\left(\frac{kk'}{K}\right)\equiv\sum_{l'-l} m_{\alpha\beta}(lk;l'k')\exp\{ik(x(l'k')-x(lk))\}, \tag{49}$$

$$a_{\alpha\beta}\left(\frac{kk'}{K}\right)\equiv\sum_{l-l'} a_{\alpha\beta}(lk;l'k')\exp\{ik(x(l'k')-x(lk))\} \tag{50}$$

The same phase factors were also chosen in the matrix of coulomb coefficients, which given as [31] and [32].

$$Q_{\alpha\beta}\left(\frac{kk'}{K}\right)=+\frac{4\pi}{va}\frac{k_{\alpha}k_{\beta}}{K^{2}}\left[1-\exp\left(\frac{-k^{2}}{4R^{2}}\right)\right]-\frac{\pi}{vaR^{2}}\sum_{h\neq 0}\left(k_{\alpha}+\tau_{\alpha}(h)\right)\left(k_{\beta}+\tau_{\beta}(h)\right)$$
$$G\left(\frac{\left|k+\tau(h)\right|^{2}}{4R^{2}}\right)\exp\left(\tau(h)(x(k)-x(k'))\right) \tag{51}$$
$$+R^{3}\sum_{l'}H_{\alpha\beta}\left(R(x(l'k'))-x(k))\right)\exp(k(x(l'k')-x(k)))$$

(the regular part) and $B_{\alpha\beta}\left(\frac{kk'}{K}\right)\equiv Q_{\alpha\beta}\left(\frac{kk'}{K}\right)-\frac{4\pi}{va}\frac{k_{\alpha}k_{\beta}}{K^{2}}$ (52)

(matrix including the divergent microscopic field). Some authors use for coulomb coefficients the notations $C_{\alpha\beta}\left(\frac{kk'}{K}\right)$ meaning just as equation 11b but with opposite sign C = - B. In the above formula $\tau(h)\equiv h_1b_1+h_2b_2+h_3b_3$, are the reciprocal lattice vectors, R is the convergence parameter, G and H are defined by G(x) = exp (-x) /x.

$$H_{\alpha\beta}(x)\equiv\frac{\partial^{2}}{\partial x_{\alpha}\partial x_{\beta}}H\left(|x|\right);\quad with\quad H(x)\equiv\frac{2}{\sqrt{\pi}}\frac{1}{x}\int_{x}^{\infty}e^{-t^{2}}dt \tag{53}$$

In the sums over h (reciprocal space) we omit the term h = (0, 0, 0); in the sum over l (direct space), if simultaneously l = (0,0,0) and k=k', we replace in the corresponding term the function

$H_{\alpha\beta}(x)$ by $H^{0}_{\alpha\beta}(x)$ defined as $H^{0}_{\alpha\beta}(x)\equiv\frac{4}{3\sqrt{\pi}}\delta_{\alpha\beta}$.

The total dynamical matrix is given by

$$C(k)=C^{sr}(k)-M^{-\frac{1}{2}}(e+N^{+})(I-Ba)^{-1}B(e+N)M^{-\frac{1}{2}}, \tag{54}$$

(With I standing for unit matrix) and we find it's eigen frequencies and eigen vectors by solving the eigen problem

$$(C(k)-\omega^{2}I)v=0 \tag{55}$$

For each wave vector k we obtain 6 Eigen frequencies $\omega_j(k)$, $where\, j = i, 2, 3, \ldots .6$ and each eigen frequency belongs an eigen vector $v_a\left(\frac{k}{kj}\right)$. The Eigen vector can be chosen so that they satisfy orthogonality and closure relations.

$$\sum_{k\alpha} v_\alpha^*\left(\frac{k}{kj}\right) v_\alpha\left(\frac{k}{kj'}\right) = \delta_{ij},$$
$$\sum_{j} v_\alpha^*\left(\frac{k}{kj}\right) v_\beta\left(\frac{k'}{kj}\right) = \delta_{kk'}\delta_{\alpha\beta} \qquad (56)$$

The atomic displacement in the mode kj is then given as

$$u_\alpha(lk) = \frac{v_\alpha\left(\frac{k}{kj}\right)}{\sqrt{M_k}} \exp\left(-i\omega_j(k)t + ik\, x(lk)\right) \qquad (57)$$

From the known Eigen vectors v, we can determine the dipole amplitudes $p_\alpha\left(\frac{k}{kj}\right)$ as

$$p = (I - aB)^{-1}(e + N)M^{-\frac{1}{2}} v \qquad (58)$$

and from the dipoles on lattice sites

$$p_\alpha(lk) = p_\alpha\left(\frac{k}{kj}\right) \exp\left(-i\omega_j(k)t + ik\, x(lk)\right) \qquad (59)$$

If the deformabilities and polarizabilities vanishes

$$m_{\alpha\beta}(lk; l'k') = 0, \qquad a_{\alpha\beta}(lk; l'k') = 0, \qquad (60)$$

Then the deformation dipole model becomes the rigid ion model. The dynamical matrix (equation 17) is in this case simplified:

$$C(k) = C^{sr}(k) - M^{-\frac{1}{2}} eBeM^{-\frac{1}{2}} \qquad (61)$$

3.3.2 Shell Model

The most widely used among the different lattice dynamical models of interatomic interactions in ionic crystals and compound semiconductors has been the well known shell model of Dick and Overhauser [3] and Cohran [4]. In this model, the ions are assumed to be polarizable and mechanically deformable and the atomic vibrations are described as the motion of the system of cores and massless charged electron shells, bound to the respective cores by harmonic force constants. The dynamical matrix corresponding to the shell model is given as [5].

$$D(\vec{q}) = (\boldsymbol{R} + \boldsymbol{ZCZ}) - (\boldsymbol{T} + \boldsymbol{ZCY})(\boldsymbol{S} + \boldsymbol{K} + \boldsymbol{YCY})^{-1} \tag{62}$$

Where **R**, **T** and **S** are the short range core-core, core-shell and shell-shell interaction matrices of order (3n x 3n). **Z**, **Y** and **K** are the diagonal matrices representing ionic and shell charges and core shell force respectively.

The shell model has been found quite successful in describing the phonon spectra and other dynamical properties of a wide class of solids in general. However, some of the additional features in the phonon dispersion curves, which results from many body effects, deformation of the electronic charge and bonds, breathing motion of the electron shells etc. could not be accounted by the shell model [20]. Several extension of the shell model have been made to incorporate the above effects in both RIM and SM for better predictions of phonon properties. In the present thesis, we are however mostly concerned about the successful extension of RIM to incorporate the special features of phonon properties of ionic and semiconducting compounds which are rich in covalency. Therefore to incorporate these effects the model deformation bond approximation, which is the simplified version of deformation dipole model.

3.3.3 Deformation Dipole Model

The development of the deformation dipole model (DDM) is based on the postulate given by Hardy and his collaborators [6,18, 33-38] according to which some types of short range polarization mechanism is considered to explain the values of Szigeti effective charge [39,40] in binary crystals. Thus, the overlap between the neighbouring ions alters when they are relatively displaced. This alteration in charge distribution in the overlap region is described formally in terms various multipoles, of which only the dipoles are retained in DDM and are considered on the ions themselves.

An examination of the framework of DDM reveals that there are three types of dipole moments. One of them, which this method considers is the displacement dipole produced as a result of the displacement of ion as a rigid sphere. This type of dipoles gives rise to the Coulomb potential $\Phi^{C}\left(\vec{r}\right)$, which has already been discussed by Kellerman [41]. The second type is the polarization dipole moment, which owes to origin to the deformation of the electronic charge cloud of an ion (lk) caused by the external electric field, $\vec{E}$ that corresponds to an effective electric field. Finally, the dipoles of third kind are produced due to slight distortion in the electron cloud about a given ion by its overlap with the charge distributions of the neighbouring ions. Hence the total dipole induced at the site (lk) can be expressed as [42, 43, 44, 45]

$$P_{\alpha}(lk)=\sum_{\beta} e_{\alpha\beta}(k)u_{\beta}(lk)+\sum_{l'k'\beta} m_{\alpha\beta}(lk;l'k')u_{\beta}(l'k')+\sum_{l'k'\beta} a_{\alpha\beta}(lk;l'k')E_{\beta}^{eff}(l'k') \qquad (63)$$

Where E_{β}^{eff} is the effective field on the site (l'k'). In equation (63), the first term is due to static ionic charge on cation and the interaction is of Coulomb type. This matrix is contributed by the displacement dipole. The matrix m with blocks m (lk, l'k') is not symmetric in $(lk)\rightarrow(l'k')$ but it satisfies the condition of translational invariance. This matrix is contributed by the ionic deformabilities and is defined as [44, 45].

$$m(1;2)=\frac{1}{3}\begin{bmatrix} -\gamma_1 & -\gamma_3 & -\gamma_3 \\ -\gamma_3 & -\gamma_1 & -\gamma_3 \\ -\gamma_3 & -\gamma_3 & -\gamma_1 \end{bmatrix} \qquad (64)$$

$$m(2;1)=\frac{1}{3}\begin{bmatrix} \gamma_2 & \gamma_4 & \gamma_4 \\ \gamma_4 & \gamma_2 & \gamma_4 \\ \gamma_4 & \gamma_4 & \gamma_2 \end{bmatrix} \qquad (65)$$

where $\gamma_{j=}\left(j=1,4\right)$ are the deformability parameters [46].

The last term is due to the electric polarizabilities and the matrix **a** with blocks a (lk; l'k') is symmetric but does not obey the translational invariance. The local electric polarizabilities are defined as

$$a(1;1)=\begin{bmatrix}\alpha_1 & 0 & 0\\ 0 & \alpha_1 & 0\\ 0 & 0 & \alpha_1\end{bmatrix} \tag{66}$$

$$a(2;2)=\begin{bmatrix}\alpha_2 & 0 & 0\\ 0 & \alpha_2 & 0\\ 0 & 0 & \alpha_2\end{bmatrix} \tag{67}$$

and the non local ones

$$a(1;2)=\begin{bmatrix}\alpha_3 & \alpha_4 & \alpha_4\\ \alpha_4 & \alpha_3 & \alpha_4\\ \alpha_4 & \alpha_4 & \alpha_3\end{bmatrix} \tag{68}$$

3.3.4 Deformation Bond Approximation Model

The rigid ion model can in some cases provide a valid interpretation scheme: if it uses a sufficient number of parameters and if the latter are sagaciously fitted. Not physical meaning, however can be ascribed to these quantities because the model, instead of taking into account the polarization of electronic orbitals with core displacements, only simulates it's effect by extending the description of the short range forces. It was seen in [44] that the deformation dipole model, if formulated with sufficient generality, is formally equivalent to the shell model in the case of ionic and semi-ionic crystals. However, two simple assumptions, which in general do not affect the generalities of the model, make it simpler and handy. The simplification consists:

(i) to reduce the number of independent "deformabilities" and

(ii) to neglect the "non local electric polarizabilities".

The above two general assumptions on the general deformation-dipole model are called the deformable bond approximations (DBA) [44]. In the case of Zinc blende structure, it represents a model with 15 independent parameters: "static ionic charge", two "deformabilities", two "local electric polarizabilities", and 10 short range coupling parameters extending to second neighbors.

As a consequence of the T_d^4 symmetry, the matrices of short range coupling coefficients take the form

$$\Phi(1;2)=\begin{bmatrix} A & B & B \\ B & A & B \\ B & B & A \end{bmatrix}; \tag{69}$$

$$\Phi(1;1')=\begin{bmatrix} C_1 & D_1 & E_1 \\ D_1 & C_1 & E_1 \\ -E_1 & -E_1 & F_1 \end{bmatrix}; \tag{70}$$

$$\Phi(2;2')=\begin{bmatrix} C_2 & D_2 & -E_2 \\ D_2 & C_2 & -E_2 \\ E_2 & E_2 & F_2 \end{bmatrix}; \tag{71}$$

The electric polarizability tensor turns out to be

$$\alpha_{\gamma\nu}(Zn;Zn)=\alpha_1\delta_{\gamma\nu} \qquad a_{\gamma\nu}(S;S)=\alpha_2\delta_{\gamma\nu} \tag{72a and 72b}$$

(local polarizabilities) and

$$a(1;2)=\begin{bmatrix} \alpha_3 & \alpha_4 & \alpha_4 \\ \alpha_4 & \alpha_3 & \alpha_4 \\ \alpha_4 & \alpha_4 & \alpha_3 \end{bmatrix} \tag{72c}$$

(non local polarizabilities); the mechanical polarizability or deformability is

$$m(1;2)=\frac{1}{3}\begin{bmatrix}-\gamma_1 & -\gamma_3 & -\gamma_3\\ -\gamma_3 & -\gamma_1 & -\gamma_3\\ -\gamma_3 & -\gamma_3 & -\gamma_1\end{bmatrix}, \qquad (73)$$

$$m(2;1)=\frac{1}{3}\begin{bmatrix}+\gamma_2 & +\gamma_4 & +\gamma_4\\ +\gamma_4 & +\gamma_2 & +\gamma_4\\ +\gamma_4 & +\gamma_4 & +\gamma_2\end{bmatrix}, \qquad (74)$$

and tensor of the static ionic charge is reduced to a scalar:

$$e_{\mu\nu}(Zn)=+q_{\mu\nu}, \qquad e_{\mu\nu}(S)=-q_{\mu\nu} \qquad (75)$$

These 19 parameters (69) to (75) define the deformation dipole model for a crystal of a Zinc blende structure. In all numerical calculation of the present work we will impose on them assumptions

$$\begin{gathered}\alpha_3=\alpha_4=0,\\ \gamma_3=\gamma_1, \quad \gamma_4=\gamma_2\end{gathered} \qquad (76\ \&\ 77)$$

Calling equation (5 and 6) deformable bond approximation.

The assumption (76 and 77) was inspired by work of Von Hipple [46] and Birman [47]; Von Hipple suggested considering the crystal as a lattice of dipoles associated with chemical bonds, Birman added the hypothesis that every dipole follows the instantaneous direction of the bond and that it's magnitude depends only on the actual distance of the atom at it's ends. To elucidate this, let us consider a diatomic molecule AB, it's dipole moment can be written

$$\mathrm{p}=p(r)\frac{\mathrm{r}}{|\mathrm{r}|} \qquad (78)$$

In equilibrium, it is $r = r_0$, and we can define the static ionic charge q through the equilibrium dipole moment of the molecule:

$$p(r_0) = -q(r_0) \tag{79}$$

If the atoms A and B are displaced from the equilibrium by a small amount **u**,

$$\mathrm{r} = \mathrm{r}_0 + \mathrm{u}(B) - \mathrm{u}(A). \tag{80}$$

We develop p(r) in to series,

$$p(r) = p(r_0) + \left(\frac{\partial p}{\partial r}\right)_{r_0} \left(|r| - |r_0|\right) + \dots \tag{81}$$

and define coefficient γ as

$$\left(\frac{\partial p}{\partial r}\right)_{r_0} \equiv -q - \gamma \tag{82}$$

Expressing r and $\frac{1}{r}$ as a function of r_0 and **u** ,the equation (78) takes the form

$$\mathrm{p} = p(r_0)\frac{\mathrm{r}_0}{|\mathrm{r}_0|} + q\mathrm{u}(A) - q\mathrm{u}(B) + \gamma\frac{\mathrm{r}_0\left[\mathrm{r}_0\left(\mathrm{u}(A) - \mathrm{u}(B)\right)\right]}{|\mathrm{r}_0|^2} \tag{83}$$

The dipole moment of a molecule AB may thus be interpreted as composed of its permanent or equilibrium moment, of that created by the displacements of punctual charges +q, and of the dipole created by the deformation of the charge distribution. The parameter γ can be interpreted as mechanical polarizability of the bond. And it is natural split it into two components $\gamma = \gamma_1 + \gamma_2$. Thereby, situating the corresponding parts of equation at the sites A and B. On expressing the last term of equation (82) in the DDM formalism it is found that the deformability matrix for molecule AB has the form of equation (74) and simplified by the condition in equation (76 and 77). In other words, the assumption in equation (76 and 77) means that only that part of the bond has been taken in to account, which is parallel with the equilibrium directions of the bond. The dynamical matrix corresponding to DDM therefore can be written as,

$$\mathrm{C}\left(\vec{q}\right)=\mathrm{C}^{\circ}\left(\vec{q}\right)-\mathrm{M}^{-\frac{1}{2}}\left(\mathrm{e}+\mathrm{N}^{+}\right)\left(\mathbf{I}-\mathrm{B}a\right)^{-1}\left(\mathrm{e}+\mathrm{N}\right)\mathrm{M}^{-\frac{1}{2}} \tag{84}$$

Where, **I** stands for unit matrix. $\mathrm{C}^{SR}\left(\vec{q}\right)$ is the short range matrix and defined as

$$C^{SR}_{\alpha\beta}(\vec{q})=\frac{1}{\sqrt{M_k M_{k'}}}\sum_{l-l'}\Phi_{\alpha\beta}(lk;l'k')\exp\left[i\vec{q}.\left(\vec{x}(l'k')-\vec{x}(lk)\right)\right] \tag{85}$$

The matrices N and a are the Fourier transform of the deformability and polarizability matrices, respectively are written as

$$N_{\alpha\beta}\left(\frac{kk'}{\vec{q}}\right)=\sum_{l-l'}m_{\alpha\beta}(lk;l'k')\exp\left[i\vec{q}.\left(\vec{x}(l'k')-\vec{x}(lk)\right)\right] \tag{86}$$

and

$$a_{\alpha\beta}\left(\frac{kk'}{\vec{q}}\right)=\sum_{l-l'}a_{\alpha\beta}(lk;l'k')\exp\left[i\vec{q}.\left(\vec{x}(l'k')-\vec{x}(lk)\right)\right] \tag{87}$$

respectively. The matrix B in the dynamical matrix (equation 84) is the contribution to the Coulomb coefficient. The Eigen frequencies can be obtained by solving the Eigen value problem

$$\left|\mathrm{C}\left(\vec{q}\right)-\omega^{2}\,\mathbf{I}\right|\mathrm{u}=0 \tag{88}$$

For each wave vector, $\vec{q}$ we obtain 6 eigen frequencies $\left(\omega_j\,(\vec{q}),\ j=1,2,3\ldots6\right)$

From the phonon band structure $\omega_j(q)$, it is straight forward to find the corresponding density of states as it gives the information of phonons in whole Brillouin zone (BZ). In order to obtain the information about the whole phonon spectrum, Brillouin-zone scanning is necessary. Such a scanning consists in $D_{\alpha\beta}\begin{pmatrix} q \\ kk' \end{pmatrix}$ -matrix diagonalization over the three dimensional net of wave vector $\boldsymbol{q} = \left(\frac{a^*}{n_1}, \frac{b^*}{n_2}, \frac{c^*}{n_3}\right)$, at n_1, n_2, n_3 = - N,...., N. In total, this includes $N_i = (2N + 1)^3$ points in Brillouin zone. The phonon density of states (DOS) is determined by summation over all the phonon states and is defined by

$$g(\omega) = D' \int_{BZ} \sum_j \delta\left[\omega - \omega_j(\boldsymbol{q})\right] dq = D' \int_{BZ} \sum_{jp} \delta\left[\omega - \omega_j(\boldsymbol{q})\right] dq_p \tag{89}$$

Where, BZ corresponds to the Brillouin zone, D' is a normalization constant such that $\int g(\omega)\, d\omega = 1$; that is, $g(\omega)\mathrm{d}\omega$ is the fraction of phonons which have energies within a range from ω to $\omega + \mathrm{d}\omega$. '$p$' is the mesh index characterizing '$\boldsymbol{q}$' in the discretized irreducible Brillouin zone and $\mathrm{d}\boldsymbol{q}_p$ provides the weighting factor corresponding to the volume of p^{th} mesh in $\boldsymbol{q}$-space. Partial atomic density of state (PDOS) shows the contribution of different atoms to phonon density of states (DOS) and therefore, it essentially helps in understanding the atomic level contribution to the total phonon DOS. It is defined as

$$g(\omega) = D' \sum_{jp} \delta\left(\omega - \omega_j(\boldsymbol{q})\right) \frac{\left|\xi_j(\boldsymbol{q})\right|^2}{\sum_{jp}\left|\xi_j(\boldsymbol{q})\right|^2} \tag{90}$$

For a solid at a temperature T, the mean number of phonons with energy $\hbar\omega_j(\boldsymbol{q})$ is given by the Bose-Einstein distribution, $n_{jq}(T) = \left[\exp\frac{(\hbar\omega(\boldsymbol{q}))}{K_B T} - 1\right]^{-1}$. The mean square displacement of a single quantum mechanical harmonic oscillator, $\langle u^2 \rangle = \left(\frac{\hbar}{m\omega}\right)\left(n + \frac{1}{2}\right)$ can easily be generalized to that of a single atom in the direction i as

$$\left\langle u_{ki}^2 \right\rangle = \left[\frac{V}{2\pi^3}\right] \cdot \left(\frac{\hbar}{m_k}\right) \sum \int_{BZ} \left|\varepsilon_{jki}(\boldsymbol{q})\right|^2 \cdot \left[\frac{\left\{n_{jq}(T) + \frac{1}{2}\right\}}{\omega_j(\boldsymbol{q})}\right] \cdot d\boldsymbol{q} \tag{91}$$

It can be seen from the above expression that light atoms vibrating at low frequencies exhibit large zero point motions. The off-diagonal elements $\left\langle \bar{u}_{ki}\,\bar{u}_{kj} \right\rangle$ can be calculated in a similar way. The thermal and zero point motion of the atoms are often described using the matrix of anisotropic temperature factors, $\bar{B}$. For an atom ***k***, it is defined by

$$\bar{B}_{ij}\left(\bar{k}\right)=8\pi^2\left\langle \bar{u}_{ki}\,\bar{u}_{kj} \right\rangle \tag{92}$$

The theory of lattice dynamics described above allows us to determine the phonon frequencies in the harmonic approximation. Anharmonic effects are relatively small at low temperature in most crystals and become more important at high temperatures. The thermodynamic properties of a crystal may be calculated in the quasiharmonic approximations[1-3]. In quasiharmonic approximation the vibrations of atoms at any finite temperature are in principle, assumed to be harmonic about their mean positions appropriate to that temperature. The free energy, in three dimensional cases, is a function of temperature *T* and the volume *V* and the equation of state is given by

$$P=-\left(\frac{\partial F}{\partial V}\right)_T \tag{93}$$

Where, $F^P(T)=\frac{K_B T}{N_t}\sum_{jp}\ln\left(2\sinh\left(\beta_{jp}\right)\right)$. (94)

Here, $\beta_{jp}=\frac{\hbar\omega_j\left(q_p\right)}{2K_B T}$. The quantity $\hbar\omega_j\left(q_p\right)$ is the phonon energy and, $\hbar = h/2\pi$ with h and $\omega_j(\mathbf{q}_p)$ as Planck constants and phonon branch at $\mathbf{q}_p$ respectively. K_B is Boltzmann's constants and T is temperature. The internal energy U and the entropy S are given by the relations

$$U=F-T\left(\frac{\partial F}{\partial T}\right)_V=F+TS. \tag{95}$$

Here, $S(T) = \frac{1}{N_t} \sum_{jp} \beta_{jp} \coth\left(\beta_{jp}\right) - \ln\left(2\sinh\left(\beta_{jp}\right)\right)$. (96)

The Heat capacity is defined by $C(T) = \frac{1}{N} \sum_{jp} \left[\frac{\beta_{jp}}{2\sinh(\beta_{jp})} \right]^2$. (97)

The relations (eq. (94), (96), and (97)) concern with the specific values per unit cell. However, the specific heat $C_V\,(T)$ can also be expressed as

$$C_V\left(T\right) = \frac{dE}{dT} = \frac{\hbar^2}{K_B T} \int_0^{\omega_D} \frac{\omega^2 exp\left(\hbar\omega / K_B T\right)}{\left(exp\left(\hbar\omega / K_B T\right) - 1\right)^2} g\left(\omega\right) d\omega \tag{98}$$

Where $g(\omega)$ is the phonon density of states. Since the experimental measurements usually provides C_P value, which differs from C_V value at elevated temperature, the following corrections is required: $C_P = C_V + \mathrm{B}\beta^2 V_m T$, where B is the bulk modulus expressed as $\mathrm{B} = -\,V(\mathrm{d}P/\mathrm{d}V)_{V0}$, β is the thermal expansion coefficient and V_m is the molar volume at equilibrium.

3.3.4 (a) Acoustic response: The Elastic Constants

It is well known that in the long wavelength limits$\left(\vec{q} \rightarrow 0\right)$, the velocity of sound is independent of frequency. Thus, according to continuum theory of elastic waves, we find that the elastic vibrational frequencies tend to zero in such a way that $\left(\frac{\omega}{\vec{q}}\right)^2_{\vec{q}\rightarrow 0}$ attains a definite limit which is related to the elastic constants (Cij). The dynamical matrix, defined by the equations (84), gets simplified due to the deformable bond approximation, which then can be solved to derive the elastic properties. The derived constants are [47]

$$C_{11} = -\frac{A+4(C_1+C_2)}{a} + \frac{q^2(u-r)}{\pi^2 a} \tag{99}$$

$$C_{12} = \frac{A-2B+2(C_1+C_2)-4(D_1+D_2)+2(F_1+F_2)}{a} + \frac{q^2(w+S-v-t)}{\pi^2 a} \tag{100}$$

$$\begin{aligned} C_{44} = & -\frac{A+2(C_1+C_2)+2(F_1+F_2)}{a} + \frac{(v-s)(1-z\alpha)q^2 - p^2q^2\alpha - 4\pi\gamma\left(\frac{z\pi\gamma}{3}\right)}{\pi^{2a}(1-z\alpha)} \\ & + \left[2\pi B(1-z\alpha) + q^* \frac{3pq+2z\pi\gamma}{3}\right]^2 \times \left[4A(1-z\alpha)+zq^{*2}\right]^{-1} \times \left[\pi^2 a(1-z\alpha)\right]^{-1} \end{aligned} \tag{101}$$

and the piezoelectric constant is

$$\begin{aligned} C_{14} = & 2q^* \left[2\pi B(1-z\alpha) + q^* \frac{3pq+2z\pi\gamma}{3}\right] \times \left[4A(1-z\alpha)+zq^{*2}\right]^{-1} \times \left[\pi a^2(1-z\alpha)\right]^{-1} \\ & - \frac{6pq\alpha+4\pi\gamma}{3}\left[\pi a^2(1-z\alpha)\right]^{-1} \end{aligned} \tag{102}$$

with A, B, C_k, D_k, E_k, F_k, (k=1,2) as the short range parameter , $\gamma = \gamma_1 + \gamma_2$ and

$$p = \frac{15.7985}{V_\alpha},\ r = \frac{6.398}{V_\alpha},\ s = \frac{10.581}{V_\alpha},\ t = \frac{43.45}{V_\alpha}, u = \frac{8.84}{V_\alpha}$$

$$V = \frac{9.36}{V_\alpha},\ w = \frac{16.1}{V_\alpha},\ z = \frac{4p}{3V_\alpha}$$

with V_α as the volume of the unit cell are the numerical coefficient which results from the derivatives of the Coulomb coefficients.

3.3.4 (b) The Optical Response: Dielectric properties

The long wave optical response of DDM-DBA can be understood by solving the secular equation in the $(\vec{q},0,0)$ direction in the long wavelength limit (i.e.$(\vec{q} \to 0)$). This yields two distinct optical vibrational frequencies. The first one correspondence to the longitudinal optical (LO) and another to transverse optical modes (TO) modes. Their relevant expressions are

$$\omega^2_{LO} = \frac{1}{\mu}\left[-4A + \frac{q^{*2}}{\alpha + 3\left[\frac{V_a}{8\pi}\right]} \right] \tag{103}$$

and

$$\omega^2_{TO} = \frac{1}{\mu}\left[-4A + \frac{q^{*2}}{\alpha - 3\left[\frac{V_a}{8\pi}\right]} \right] \tag{104}$$

The high frequency dielectric constant is given as

$$\varepsilon_{\infty} = \delta_{\alpha\beta}\,\frac{3V_a + 8\pi(\alpha_1 + \alpha_2)}{3V_a - 8\pi(\alpha_1 + \alpha_2)} \tag{105}$$

the quantity $\alpha = (\alpha_1 + \alpha_2)$ may be identified with the electronic polarizability of the macroscopic theory. The combination

$$e^{*} = e\frac{4}{3}(\gamma_1 + \gamma_2) \tag{106}$$

has the meaning of effective charge of Szigeti. The DDM-DBA has been successfully used by Kunc et. al. [42] to calculate the phonon dispersion curves of several III-V compound semiconductors. In the present work, this model theory alongwith the rigid ion model for phosphides and antimonide has been used to calculate the phonon properties of some semiconducting compounds under compression.

3.4 Many Body Interactions Theories

In this section, we briefly describe some other model theories which have been found useful to describe the phonon properties in the semiconductors. Despite the remarkable success of SM and other theories, they are subject to some in adequacies. In view of theory of elastic constants these models have common deficiency as they lead to fulfillment of the Cauchy relations ($C_{12} = C_{44}$). This is because the polarizabilities of ions as introduced in these models, has no effect on the elastic constants and hence the LO (L) branch along $\left(\vec{q},\vec{q},\vec{q},\right)$ direction. The reasons for such shortcomings in these theories have been clearly traced by Cowley et al. [48] and Singh [20]. Also none of them gives good agreement between theoretical and experimental results on strain derivatives of dielectric constants and photoelastic constants [49].

Most of the above inadequacies are believed to arise in SM because its energy expression excludes the many body interactions. Indeed, attempt have been made to incorporate many body interaction effects in the framework of SM and they have led to several models such as deformation shell model (DSM) [50], breathing shell model (BSM) [7] and three body force shell model (TSM) [51] which take account of both deformation and displacement of the electron shell.

These model theories, as their names imply, consider additional interactions due to charge density deformations (DSM) [50] and breathing motion of the electronic shells (BSM) [7] of the ions. These effects are short range (SR) in nature and localized upto nearest neighbor only and therefore in principle, modify the SR repulsive interaction matrix **R**. The other model theory, three body force shell model (TSM) [51], includes the effects of charge transfer when the nearest neighbor ions overlap. Such an effort not only modifies the repulsive interaction matrix **R** of shell model, but also adds an additional term to the coulomb interaction matrix **C**. This effect also modifies the core and shell charges. All these effects are many body types in nature and have been proved to be useful in understanding the greater complexity and diversity of the phenomenon of lattice vibrations in non metallic solids. In the following, we discuss the silent features of DSM and BSM, including their elastic and optical response in the long wavelength limit in order to understand the effect of pressure on the lattice vibrational properties of non metallic solids and some semi-magnetic semiconductors three body force shell model (TSM) will be used. The salient features of three body force shell model will be discussed later.

In this chapter, we have discussed the model theories at length, which we use for the study of lattice vibrational properties of III-nitrides, III-phosphides and antimonide semiconducting compounds under compression. In the next two chapters, we bring out detailed discussion on determination of the model parameters and it's applications to explain phonon properties under pressure. In chapter 6 we describe the details of the three body force model which takes an account of many body interactions. This model is used here to describe the structural properties of some diluted magnetic semiconductors under high pressure.

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