Chapter - II

THE DYNAMICAL MODEL

2.1 INTRODUCTION

Since neutron scattering experiments have provided a reliable data for phonon dispersion in zinc-blende (ZB) type crystals, a considerable effort has been devoted to the theoretical studies of these crystals. Numerous model have been employed to study the lattice dynamics of various II–VI and III–V compounds having ZB type structure. A non-central force model within the framework of the shell model by Cochran has been developed for studying various lattice dynamic properties of semiconducting ternary mixed crystals, which are of general scientific and technical interest some of such crystals have wide applications in infrared and wide band detectors. Besides they can be used for thermoelectric power conversion with efficiency high enough to have practical interest in high efficiency Hall probes. Study of the lattice dynamical aspect of such crystals is, therefore of much importance from the angle of understanding the nature of their interatomic interactions. We have carefully reviewed the theoretical work is the field of lattice dynamics of mixed semiconductors by Matossi, Verleur and Barker, Chang Mitra, Elliott et al., Varshney et al., Massa et al. and Gupta et al. The model theories which have been employed for this purpose can broadly be classified in two categories (i) rigid-ion model (RIM) (ii) shell-model (SM)/deformation
dipole model (DDM). In spite of its failure to explain simultaneously the optical and dielectric behaviour of the crystals. The shell-model on other hand, being a realistic model involves a large number of parameters (usually above 15 whose evaluation require an extensive fitting of experimental data). RIM and SM/DDM and their ramifications have been developed and widely used comprehensive critical review of the model theories have been made available by several authors\textsuperscript{9-12}.

In microscopic crystal dynamics\textsuperscript{13-15} of non-metallic crystals the electronic response to core displacements as described through a non-local dielectric function, gives explicit expressions for it in terms of a complete set of equilibrium wave functions for it in terms of a complete set of equilibrium wave functions\textsuperscript{16}. Theories concerning first principle as well as second order perturbation\textsuperscript{17} calculations for such crystals met very limited success.

It was emphasized by Lowdin\textsuperscript{18} that the concept of two-body interactions is only approximate and that an appreciable part of the lattice cohesive energy can not be represented in terms of two-body interactions. Inelastic deformations this part causes deviations from Cauchy relations. Moreover, in ionic and partially ionic crystals, an ion may be polarized by the resultant electric field due to other ions in the lattice. The effect of such polarizations on the lattice energy is not in the nature of two-body interaction. In view of this fact Singh et al.\textsuperscript{19} developed a version of SM which is based on an extension of the ideas developed by Lundquist\textsuperscript{20} and originally put forward by Lowdin\textsuperscript{18}. The three-body force term incorporated in their SM by Singh et al.\textsuperscript{19} is long-
range is nature and in other words modifies the Coulombic-interaction matrix elements.

The SM which in its framework has been given a quantum mechanical justification by Cowley\textsuperscript{21} is in fact equivalent to the microscopic dipolar model (MDM) by Meshkevich and Tolpygo\textsuperscript{22}. These models do not go beyond the RIM with respect to the elastic behaviour of the solids, although the dielectric properties are very well explained. Consequently the MDM's are not capable of explaining the break down of the Cauchy relations which is considerable in most of the covalent, ionic and partially ionic crystals. In view of the difficulties of the first principles approaches and ideas put forward by some authors\textsuperscript{23} we have thought it pertinent to propose a new ramification of SM which incorporates the TBSM which are, in essence, short-range three-body forces in the second neighbour rigid-shell model (RSM) due to Cochran and co-workers\textsuperscript{24}. The TBSM which are more complicated than the two-body forces are assumed to arise from the deformations in the interbond angles. We have thought it worth while to develop a new model for such structure which takes into account the covalent nature of atomic bonds with reasonably lesser number of parameters.

2.2 THREE–BODY SHELL–MODEL (TBSM)

The theory of TBSM basically incorporates the effect of TBSM and the short-range repulsive forces up to and including the second nearest neighbours, in addition to the long-range Coulombic interactions in the framework of the RSM due to Woods et al.\textsuperscript{24} with both the ions polarizable. The general formulation of the TBSM
remains in the harmonic approximation and can be derived from the work at Cochran and his collaborators\(^1\) who have developed the framework of RSM in their pioneer work devoted to formulate a dynamical theory for a comprehensive description of the vibrational spectrum and the dielectric properties of ionic crystals and remove the drawbacks of RIM. The electronic dipole moments are determined by both long- and short-range forces and they thus have two contributions arising from various long-range electrostatic forces and the other arising from SR (or distortion) polarization mechanism. Thus the electronic polarization can be written as

\[
p_k = p_k^c + p_k^d = \mu_k + \mu_k^d
\]

where \(\mu_k\) and \(\mu_k^d\) are the electronic and distortion dipole moments which give rise to the electrical and distortion (or mechanical) polarizabilities denoted by the parameters \(\alpha_k\) and \(\alpha_d\) respectively. Thus in the frame-work of three-body shell-model (TBSM) the harmonic potential energy per unit-cell is given by

\[
\phi_{TBSM} = \phi_{SM} + \phi_{TB}
\]

\(\phi_{SM}\) and \(\phi_{TB}\) are potential energies of the binary crystal in the framework of rigid shell-model and three-body interaction. \(\phi_{SM}\) is given by

\[
\phi_{SM} = \frac{1}{2} \sum_{\ell k} \sum_{\ell' k'} \frac{Z_k Z_{k'} e^2}{r(\ell k; \ell' k')} + \frac{1}{2} \sum_k \frac{p_k}{\alpha_k}
\]

\[
- \sum_k p_k \left( E_k^m + \frac{1}{2} E_k^p \right) + \frac{1}{2} \sum_k \sum_{\ell' k'} \phi \left[ \frac{r(\ell k; \ell' k') - p_k + p_{k'}}{y_k y_{k'}} \right]
\]
where \( E_{k}^{m} \) is monopole electric field at the ion (\( \ell k \)) of monopole charge (\( Z_k e \)) due to all other ions. Similarly, \( E_{k}^{p} \) is the dipole electric field for the dipoles at the site (\( \ell k \)). The prime over the summation means the exclusion of the term \( \ell k = \ell' k' \). The first three terms in the above equation represent the electrostatic-interactions between the charges (or monopoles) and the dipoles. The last term gives the overlap repulsion. \( \alpha_k \) is the electronic polarizability. The net charge on the combination of \( k^{th} \) core and shell is given by

\[
Z_k e = (X_k e + Y_k e)
\]

where, \( X_k \) and \( Y_k \) are core and shell charges.

Equations relevant to core and shell displacements for the vibration mode \( \omega(q) \) are given by

\[
m \omega^2 U = (R + Z C Z) U + (T + Z C Y) W
\]

\[
= (T^t + Y C Z) U + (S' + Y C Y) W
\]

where \( R, T, S(S' - k) \) are q-dependent \( 3n \times 3n \) matrices (\( n \) is the number of atoms per unit cell) which describe the short-range interactions. \( T^t \) is the transpose conjugate of \( T \). \( C \) is a \( 3n \times 3n \) matrix of Coulombic coupling coefficients which are evaluated by Ewald's method. \( m, Z \) and \( Y \) are the \( 3n \times 3n \) diagonal matrices which designate the ion masses, ion
charges, and shell charges, respectively. $k$ is also the diagonal $3n \times 3n$ matrix representing the restoring force constant between the core and the shell of the ions. $U$ and $W$ are the vectors describing the ionic displacements and deformations, respectively.

Eliminating $W$ from equation (2.2b) we obtain the equation governing the motion of the ion cores

$$m \omega^2 U = (R + Z_C Z) - (T + Z_C Y) \times (S' + Y C Y)^{-1} (T^t + Y C Z) U$$

$$= D(q) U$$

(2.3)

where

$$D(q) = (R + Z_C Z) - (T + Z_C Y) \times (S' + Y C Y)^{-1} (T^t + Y C Z)$$

(2.4)

is the dynamical matrix of order $3n \times 3n$. The condition that the set of the Equation (2.3) have a non-trivial solution is that the determinant of the coefficient vanish, i.e.,

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

(2.5)

Along the symmetry directions the matrix $D(q)$ reduces to a $(2 \times 2)$ matrix leading to the characteristic equation
as the condition for the solubility. The matrix elements $D(q_{\tilde{\bm{k}}k})$, $D(q_{\tilde{\bm{k}}k'})$, $D(q_{\tilde{\bm{k}}'k})$, and $D(q_{\tilde{\bm{k}}'k'})$ are given for a zinc-blende structure. The expression for the matrix elements $D(q_{\tilde{\bm{k}}k'})$ shows a new term (underlined) which was not noticed in the earlier work on RSM.

The elements of the dynamical matrix $D(q_{\tilde{\bm{k}}k'})$ along the symmetry directions are derived Woods et al.\textsuperscript{24} as

$$D(q_{\tilde{\bm{k}}k}) = R_{11} - \frac{e^2}{f} \left[ \frac{d_1^2}{\alpha_1} + \frac{|R_{12}|^2}{R_{22}} \frac{d_2}{\alpha_2} \right] + \frac{e^2}{Vf} C_1 \left[ Z^2 - \alpha_2 \frac{d_1^2}{\alpha_1} - \alpha_1 \frac{|R_{12}|^2}{R_{22}} \frac{d_2}{\alpha_2} + 2Zd_1 \right]$$

$$+ (Z + d_1) \frac{d_2}{R_{22}} \left( C_2 R_{12}^* + C_2^* R_{12} \right) + (Z + 2d_1) \frac{Z}{V} \alpha_2 \left( C_1^2 - |C_2|^2 \right) \right]$$

$$D(q_{\tilde{\bm{k}}'k'}) = R_{22} - \frac{e^2}{f} \left[ \frac{d_2^2}{\alpha_2} + \frac{|R_{12}|^2}{R_{11}} \frac{d_1^2}{\alpha_1} \right] + \frac{e^2}{Vf} C_1 \left[ Z^2 - \alpha_2 \frac{d_1^2}{\alpha_2} - \alpha_1 \frac{|R_{12}|^2}{R_{11}} \frac{d_2^2}{\alpha_1} - 2Zd_2 \right]$$

$$- (Z - d_2) \frac{d_1}{R_{11}} \left( C_2 R_{12}^* + C_2^* R_{12} \right) + (Z - 2d_2) \frac{Z}{V} \alpha_1 \left( C_1^2 - |C_2|^2 \right) \right]$$
The C\textsubscript{1} and C\textsubscript{2} are defined as

\[ C_1 = \frac{V}{e^2} \{C_{xx}(kk)\}; \quad C_2 = \frac{V}{e^2} \{C_{xx}(kk')\} \]

and the abbreviation \( f \) is defined as

\[ f = 1 + \frac{\alpha_1 + \alpha_2}{V} C_1 + \frac{\alpha_1 \alpha_2}{V^2} (C_1^2 - |C_2|^2). \]

Here \( |C_2|^2 = C_2 C_2^* \).

The expressions for the dynamical matrix \( D(q) \) shows a new term (underlined) which was not noticed in the earlier work on RSM. The appearance of this new term is subject to the unequal treatment of the shell charge - otherwise it vanishes. In these matrix elements \( \alpha_i \) and
\( d_i \) are, respectively, the electrical and mechanical polarizabilities expressed as
\[
\alpha_i = \frac{(Y_i e)^2}{k_i + R_{ii}^0} \quad \text{and} \quad d_i = \frac{Y_i R_{ii}^0}{k_i + R_{ii}^0}, \quad i = 1, 2
\]

If \( k \to \infty \) these expressions of the matrix elements \( D(q_{ij}) \) reduce to the expressions for RIM which apply when \( \bar{q} \) is in the symmetry directions.

### 2.3 SHORT-RANGE NON-COULOMBIC INTERACTION

(Two-body interaction)

For the short-range interaction involving two-body forces be expressed two-body short-range potential energy in terms of Taylor's series:

\[
\Phi_1 = \sum_{\ell,m,n} \left[ \frac{1}{r} \left( \frac{d\Phi}{dr} \right)_{r=r_1} \left\{ \vec{r}_{\ell mn} \cdot (\vec{S}_{\ell mn} - \vec{S}_0) + \frac{1}{2} \left| \vec{S}_{\ell mn} - \vec{S}_0 \right|^2 \right\} + \frac{1}{2} \left\{ \frac{1}{r} \frac{d\Phi}{dr} \right\}_{r=r_1} \right] \times \left\{ \vec{r}_{\ell mn} \cdot (\vec{S}_{\ell mn} - \vec{S}_0) \right\}^2 \tag{2.11}
\]

\( \vec{S}_0 \) and \( \vec{S}_{\ell mn} \) are the displacements of the central ion and its first neighbour ions from their normal positions, \( \vec{r}_{\ell mn} \) represents the position coordinates of neighbouring atoms in equilibrium. \( \ell, m, n \) represents the direction cosine of the line joining the central ion and a nearest neighbour. \( r_1 \) is the nearest neighbour distance.

In our work we have considered two-body short-range interaction between the central atom and its first and second nearest neighbours. Let \( A \) be the force constant corresponding to the second
derivative of potential energy in the above expression for the first nearest neighbours i.e.

\[
\frac{e^2}{V} A = \left. \frac{d^2 \phi}{dr^2} \right|_{r=\eta} \quad (2.12)
\]

Similarly \( A_1, A_2 \) are the force constant for the second neighbours which includes two different types of similar atoms i.e.

\[
\frac{e^2}{V} A_1 = \left. \frac{d^2 \phi}{dr^2} \right|_{r=r_2} \quad (k,k) \text{ type of atoms}
\]

\[
\frac{e^2}{V} A_2 = \left. \frac{d^2 \phi}{dr^2} \right|_{r=r_2} \quad (k',k') \text{ type of atoms} \quad (2.13)
\]

2.3.1 Matrix Elements (Two-body interaction)

The first nearest neighbours are assumed to interact with central force constant \( A \) and next nearest neighbours (second) are assumed to interact with central force constants \( A_1 \) and \( A_2 \) respectively.

The following elements of the short-range interaction dynamical matrix have been obtained

\[
R_{11} = R_{XX}(\vec{q},kk) = \frac{e^2/a^3}{m_1} \left[ \frac{4}{3} A + 4A_1(1-(1-2S_x^2)(1-S_y^2-S_z^2)) \right]
\]

\[
R_{22} = R_{XX}(\vec{q},kk') = \frac{e^2/a^3}{m_2} \left[ \frac{4}{3} A + 4A_2(1-(1-2S_x^2)(1-S_y^2-S_z^2)) \right]
\]

\[
R_{11} = R_{XY}(\vec{q},kk) = \frac{e^2/a^3}{m_1} \left[ 8A_1 C_x C_y S_x S_y \right]
\]
The other combinations are obtained by cyclic permutations of indices. \( A \) is the radial force constant for the first neighbour and \( A_1 \) and \( A_2 \) are the radial force constants for the second neighbours for similar and dissimilar atoms where \( C_i = \cos \pi a \ k_i \) and \( S_i = \sin \pi a \ k_i \) where \( i = x, y, z \) and \( 2a \) is the lattice constant, and \( q = 2\pi k \).

### 2.3.2 Short-Range Non-Coulombic Interaction
(Three-body interaction)

The potential energy \( \Phi_2 \) giving rise to the TBSM has been assumed to be of the form

\[
\Phi_2 = \frac{1}{2} \left( \frac{e^2}{a^3} \right) \gamma_\theta (\delta \theta)^2
\]

(2.15)

where \( \delta \theta \) is the change in the angle under consideration and \( \gamma_\theta \) is the corresponding force constant. The term \( (e^2/a^3) \) is simply adjusted to keep force constants in the units of \( (e^2/V) \), where \( e \) is the electronic charge and \( V = (2a^3) \) is the volume of the unit cell.
The change in the angle ($\delta \theta$) is calculated geometrically Fig. (2.1) as

$$\begin{align*}
(\delta \theta) &= \left[ \frac{(\vec{S}_A - \vec{S}_O) \cdot \vec{e}_{nA}}{|\vec{OA}|} + \frac{(\vec{S}_B - \vec{S}_O) \cdot \vec{e}_{nB}}{|\vec{OB}|} \right] \\
&= (2.16)
\end{align*}$$

where $\vec{S}_A$, $\vec{S}_O$, and $\vec{S}_B$ are the displacement vectors of the respective atoms A, O and B. $\vec{e}_{nA}$ and $\vec{e}_{nB}$ are the unit vectors perpendicular to the vectors $\overrightarrow{OA}$ and $\overrightarrow{OB}$, respectively, and lying in the plane OAB [Fig. (2.1)]. The details of all such angles which have been taken into account have been given in Table (2.1) by CGW (Clark, Gazis and Wallis)\textsuperscript{25}.

Table 2.1

<table>
<thead>
<tr>
<th>Types of triangle</th>
<th>No. of triangles</th>
<th>Lable of the angles</th>
<th>No. of similar angles</th>
<th>Associated force constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>I\textsuperscript{a}</td>
<td>6</td>
<td>$\theta_1$</td>
<td>18</td>
<td>$\gamma_1$</td>
</tr>
<tr>
<td>II\textsuperscript{b}</td>
<td>12</td>
<td>$\theta_2$</td>
<td>36</td>
<td>$\gamma_2$</td>
</tr>
<tr>
<td>III\textsuperscript{c}</td>
<td>24</td>
<td>$\theta_3$</td>
<td>72</td>
<td>$\gamma_3$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Refers to the triangles formed by the bonds joining reference atom "O" which two of its first neighbours in B lattice.

\textsuperscript{b} Refers to the triangles formed by the bonds joining reference atom "O" which one of its first neighbours and the other one its second neighbours.

\textsuperscript{c} Refers to the triangles formed by the bonds joining reference atom "O" with two of its second neighbours in A lattice.
Fig. 2.1 Geometrical interpretation of bond-bending interaction.
2.3.3 Matrix Elements (Three-body interaction)

The matrix elements for three-body interaction are as follows:

\[
R_{11} = R_{XX}(\mathbf{q}_{kk}) = \frac{(e^2/a^3)}{m_k} \left[ 12\gamma_1 \{14 - (1 - 2S^2_x)(1 - 2S^2_y) - (1 - 2S^2_x)(1 - 2S^2_z) + 4(1 - 2S^2_x) \times (1 - 2S^2_z) \} + 2\gamma_2 \{14 + 2(1 - 2S^2_x)(1 - 2S^2_z) \} + 2\gamma_3 \{6 - 2((1 - 2S^2_x)(1 - 2S^2_y) + (1 - 2S^2_x)(1 - 2S^2_z) + (1 - 2S^2_x)) \} \right]
\]

\[
R_{11} = R_{XY}(\mathbf{q}_{kk}) = \frac{(e^2/a^3)}{m_k} [8\gamma_1 \{S_xC_xS_yC_y + i(2S^2_y - 2S^2_x)S_zC_z \} + 8\gamma_2 \{i(2S^2_x - 2S^2_z)S_zC_z \} + 8\gamma_3 S_xC_xS_yC_y]
\]

\[
R_{12} = R_{XX}(\mathbf{q}_{kk'}) = -\left(\frac{e^2/a^3}{\sqrt{m_1m_2}} \right) [32(\gamma_1 + \gamma_2)(C_xC_yC_z + iS_xS_yS_z)]
\]

\[
R_{12} = R_{XY}(\mathbf{q}_{kk'}) = -\left(\frac{e^2/a^3}{\sqrt{m_1m_2}} \right) [16\gamma_1(S_xS_yC_z + iC_xC_yS_z)].
\]

2.3.4 Matrix Elements (Two-body and three-body interactions)

The following elements of the two-body and three-body interaction dynamical matrix have been obtained. The matrix elements can be reduced to those for alkali halides, if we treat complex quantities as the real ones. In equation (2.7)-(2.10)

\[
R_{11} = R_{XX}(\mathbf{q},kk) = \frac{e^2}{V} \left[ \frac{4A}{3} + 4A_1\{2S^2_x + (1 - 2S^2_x)(S^2_y + S^2_z) \} \right]
\]
\[ R_{12} = R_{XX}(\vec{q}, \vec{k} \vec{k}') = -\frac{e^2}{V} \left[ \left( \frac{4A}{3} + 32\gamma_1' + 2S_1 \right)(C_x C_y C_z + i S_x S_y S_z) \right] \]  \hspace{1cm} (2.18b)

Other elements of the short-range force matrix are

\[ R_{XY}(\vec{q}, \vec{k} \vec{k}') = \frac{e^2}{V} \left[ 8A_1 S_x C_x S_y S_y + 8\gamma_1' S_x C_x S_y S_y + i (2S_2 - 2S_2^2) S_y S_z \right] \]

\[ + 8\gamma_2' \{ 0 + i (2S_2^2 - 2S_2^2) S_y S_z \} + 8\gamma_2' S_x C_x C_y C_y \]  \hspace{1cm} (2.18c)

\[ R_{XY}(\vec{q}, \vec{k} \vec{k}') \text{ can be written just by replacing } \vec{k} \text{ by } \vec{k}' \text{ in } R_{XY}(\vec{q}, \vec{k} \vec{k}) ; \]

\[ R_{XY}(\vec{q}, \vec{k} \vec{k}') = \frac{e^2}{V} \left[ \frac{4A}{3} - 16\gamma_1' (S_x S_y C_z + i C_x C_y S_z) \right] , \]  \hspace{1cm} (2.18d)

where \( \gamma_1, \gamma_2 \) and \( \gamma_3 \) are substituted for \( 4\gamma_1/9a^2 \), \( \gamma_2/3a^2 \) and \( \gamma_3/a^2 \) for brevity.

Initially \( \gamma_1, \gamma_2 \) and \( \gamma_3 \) are the three force constants associated with the corresponding angle \( \theta_1, \theta_2 \) and \( \theta_3 \). Other elements due to such forces can be written by changing Cartesian indices in cyclic order, and using the relations as above mentioned.

The solution of the characteristic equation \([\text{Eq. (2.6)}]\) at wave vector \( q = 0 \) is of special interest, particularly for examining the capacity of TBSM to describe the optical behaviour of the solids. In the
frame work of TBSM, phonon frequencies of the optical modes at $q = 0$ (zone-centre) are

$$\mu \omega_{LO}^2 = \left[ R_0' + \frac{8\pi (Z'e)^2}{3V f_L} \right], \quad (2.19)$$

$$\mu \omega_{TO}^2 = \left[ R_0' - \frac{4\pi (Z'e)^2}{3V f_T} \right], \quad (2.20)$$

where

$$R_0' = R_0 - e^2 \left( \frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right),$$

$$R_0 = \frac{e^2}{V} \left[ \frac{4A}{3} + 32\gamma_1' + 32\gamma_2' \right],$$

$$Z' = Z + d_1 - d_2,$$

$$f_L = 1 + \frac{8\pi}{3V},$$

$$f_T = 1 - \frac{4\pi}{3V}, \quad (2.21)$$

and $\alpha = \alpha_1 + \alpha_2$ (see Woods et al. and Cowley)\textsuperscript{24}. Now solution of new algebraic steps gives us

$$\mu \omega_{LO}^2 = R_0' \left[ 1 + \frac{8\pi}{3V} (\alpha + \alpha_1) \right] \left[ 1 + \frac{8\pi}{3V} \alpha \right]^{-1}, \quad (2.22)$$

$$\mu \omega_{TO}^2 = R_0' \left[ 1 - \frac{4\pi}{3V} (\alpha + \alpha_1) \right] \left[ 1 - \frac{4\pi}{3V} \alpha \right]^{-1}, \quad (2.23)$$

We have used equations (2.19) and (2.20), where $\mu$ is the reduced mass and $\alpha_1$ substituted for $(Z'e)^2/R_0'$ for brevity.
If we consider a relation \( \frac{P}{E} = \frac{(\alpha + \alpha_1)}{V} \) between polarization and effective field \( E \) and make use of the adiabatic approximation, the term \( \alpha_1 \) does not appear in the above relation. The use of adiabatic approximation in the present treatment is equivalent to the assumption that the electronic shells, moving much more faster than the cores due to their lighter masses, see the cores as being fixed in position at any given instant. This then enables us to identify \( \alpha \) and \( \alpha_1 \), respectively, as the electronic polarizability and the ionic polarizability. One can then relate the \( \alpha \) to the high frequency dielectric constant \( (\varepsilon_\infty) \) and the total polarizability \( (\alpha + \alpha_1) \) to the static dielectric constant \( (\varepsilon_0) \) through

\[
\frac{4\pi}{3V} \alpha = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}; \quad \frac{4\pi}{3V} (\alpha + \alpha_1) = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}, \tag{2.24}
\]

which are, respectively, the Lorentz-Lorentz (LL) and Clausius-Mossoti\(^{25a}\) (CM) relations. With the help of the LL and CM relations one can obtain the famous Lyddane, Schs and Teller (LST) relations\(^{26}\)

\[
\frac{\omega_{2O}^2}{\omega_{TO}^2} = \frac{\varepsilon_0}{\varepsilon_\infty}, \tag{2.25}
\]

where

\[
\varepsilon_0 = \left[ 1 + \frac{8\pi}{3V} (\alpha + \alpha_1) \right] \left[ 1 - \frac{4\pi}{3V} (\alpha + \alpha_1) \right]^{-1},
\]

\[
\varepsilon_\infty = \left[ 1 + \frac{8\pi}{3V} \alpha \right] \left[ 1 - \frac{4\pi}{3V} \alpha \right]^{-1} = \frac{f_L}{f_T},
\]
Using equations (2.19) and (2.20), the splitting of the optical phonons comes out to be

\[
\mu (\omega_{LO}^2 - \omega_{TO}^2) = \frac{4\pi}{V} \frac{(Z'e)^2}{f_L f_T} = \frac{4\pi}{9\sqrt{V \varepsilon_0}} (Z'e)^2 (\varepsilon_\infty + 2)^2
\]  
\tag{2.26a}

Substituting LST relations (2.25) in equation (2.26a), we obtain\textsuperscript{21,26}

\[
(\varepsilon_0 - \varepsilon_\infty) = \frac{4\pi(Z'e)^2}{9\sqrt{V \varepsilon_0 \mu \omega_{TO}^2}} (\varepsilon_\infty + 2)^2
\]  
\tag{2.26b}

Similarly using LL and CM relations in equation (2.23), we get

\[
\mu \omega_{TO}^2 = R'_0 \left( \frac{\varepsilon_\infty + 2}{\varepsilon_0 + 2} \right),
\]  
\tag{2.27}

\[
\omega_S^2 = \omega_{TO}^2 \left( \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2} \right),
\]  
\tag{2.28}

where \( \omega_S = \sqrt{R'_0 / \mu} \) represents a unique infrared dispersion frequency. This is also known as the second LST relation. If equations (2.26b) and (2.28) are compared with those of Szigeti\textsuperscript{26,27} one conclude that equation (2.26b) is in principle the same Szigeti\textsuperscript{26,27} whereas equation (2.28) is analogous to that obtained by Szigeti\textsuperscript{26,27} with the difference the replacement of \( R_0 \) by \( R'_0 \) equation (2.21).

2.4 LONG-RANGE COULOMBIC INTERACTION

The expression for the matrix elements due to long-range coulombic interactions were first derived by Kellerman\textsuperscript{28} for Coulombic part. Cochran obtained Coulombic-matrix elements for diamond structure and Kellerman\textsuperscript{28} derivation modified matrix elements for coulombic part. Merten extended Ewald's\textsuperscript{25} sum method for obtaining
such expressions in the case of zinc-blende structure. The expressions were also used by Rajgopal and Srinivasan\textsuperscript{30} and Banerjee and Varshani\textsuperscript{31} for studying the lattice dynamics of zinc-blende lattice. The expressions are as follows by Merten\textsuperscript{32}.

For $\bar{q} = 0$

$$S_{xy}^{c}(\bar{q}, kk') = \frac{1}{\sqrt{m_k m_{k'}}} \frac{Z_k Z_{k'} e^2}{V_a} \left( \frac{4\pi}{3} \delta_{xy} \right)$$  \hspace{1cm} (2.29)

For $\bar{q} \neq 0$

$$R_{xy}^{c}(\bar{q}, kk') = \frac{Z_k e^2}{m_k V_a} \left( -G_{xy}(kk') + H_{xy}^\ell + \frac{8}{3\sqrt{\pi}} \varepsilon^3 \delta_{xy} \right)$$  \hspace{1cm} (2.30)

$$S_{xy}^{c}(\bar{q}, kk') = \frac{Z_k Z_{k'} e^2}{\sqrt{m_k m_{k'}} V_a} (G_{xy}(kk') - H_{xy}^m)$$  \hspace{1cm} (2.31)

$$V_a = \text{Volume of the unit cell} = 2a^3$$

where

$$G_{xy}(kk) = 4\pi \sum_{\mathbf{h}} \frac{\left(\bar{h}_x + \bar{q}_x\right)\left(\bar{h}_y + \bar{q}_y\right)}{|\bar{h} + \bar{q}|^2} \exp \left( -\frac{\pi^2}{4\varepsilon^2} |(\bar{h} + \bar{q})|^2 \right)$$  \hspace{1cm} (2.32)

$$G_{xy}(kk') = 4\pi \sum_{\mathbf{h}} \frac{\left(\bar{h}_x + \bar{q}_x\right)\left(\bar{h}_y + \bar{q}_y\right)}{|\bar{h} + \bar{q}|^2} \exp \left( -\frac{\pi^2}{4\varepsilon^2} |(\bar{h} + \bar{q})|^2 \right) \exp (i\pi/2(h_x + h_y + h_z))$$  \hspace{1cm} (2.33)

$$H_{xy}^\ell = 2 \sum_{\ell} \left( -f(\ell) \delta_{xy} + g(\ell) \frac{\ell_x \ell_y}{|\ell|^2} \right) \cos \pi \cdot \bar{q} \cdot \bar{\ell}$$  \hspace{1cm} (2.34)

$$H_{xy}^n = 2 \sum_{\bar{n}} \left( -f(\bar{n}) \delta_{xy} + g(\bar{n}) \frac{n_x n_y}{|\bar{n}|^2} \right) \exp i\pi \bar{q} \cdot \bar{n}$$  \hspace{1cm} (2.35)
\[ f(\tilde{\ell}) = \frac{2}{\sqrt{\pi}|\tilde{\ell}|^2} \exp\left(-\varepsilon^2 |\tilde{\ell}|^2\right) + \frac{\psi(\varepsilon \ell)}{|\tilde{\ell}|^3} \] (2.35a)

\[ f(\bar{n}) = \frac{2}{\sqrt{\pi}|\bar{n}|^2} \exp\left(-\varepsilon^2 |\bar{n}|^2\right) + \frac{\psi(\varepsilon \bar{n})}{|\bar{n}|^3} \] (2.35b)

\[ g(\tilde{\ell}) = 3f(\tilde{\ell}) + \frac{4\varepsilon^2}{\sqrt{\pi}} \exp\left(-\varepsilon^2 |\tilde{\ell}|^2\right) \] (2.35c)

\[ g(\bar{n}) = 3f(\bar{n}) + \frac{4\varepsilon^2}{\sqrt{\pi}} \exp\left(-\varepsilon^2 |\bar{n}|^2\right) \] (2.35d)

and,

\[ \psi(\varepsilon \ell) = 1 - \frac{2}{\sqrt{\pi}} \int_0^\infty \exp\left(-\xi^2\right) d\xi \] (2.35e)

where, \( \varepsilon \) is a arbitrary parameter generally taken as unity, so that the two series \( \sum_\tilde{\ell} \) and \( \sum_{\bar{n}} \) converge rapidly. It may be noted that the summation over \( \tilde{\ell}, \bar{\ell} \) and \( \bar{n} \) are subject to the constraints given by (2.36a), (2.36b) and (2.36c). The quantities \( n_x, n_y, n_z \) and \( \ell_x, \ell_y, \ell_z \) are defined as in (1.19) such that

\[ n_x = \ell_x - \frac{1}{2} \] (2.36a)

\[ n_y = \ell_y - \frac{1}{2} \] (2.36b)

\[ n_z = \ell_z - \frac{1}{2} \] (2.36c)

where \( \ell_x, \ell_y \) and \( \ell_z \) is even and \( n_x, n_y \) and \( n_z \) is odd. The other elements of the matrix \( S_{xy}^C(q_i, kk') \) are generated by the cyclic permutation of the indices \( x, y \) and \( z \).
2.5 THE ELASTIC CONSTANTS AND MODEL PARAMETERS

If the secular equation developed for lattice vibration of a crystal using a definite force model is solved for longwavelength ($q \to 0$). This type of relations was initially proposed and developed by Born and Blackmann$^{32a}$ and has been discussed in detail in the book "Dynamical theory of Crystal Lattices" by Born and Huang$^{33}$. We thus, obtain the following expressions for three elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ are obtained in terms of the model parameters for zinc-blende structure crystals.

\begin{align*}
2aC_{11} &= \frac{e^2}{V} \left[ \frac{A}{3} + 2A_1 + 2A_2 + 12\gamma_1' + 8\gamma_2' + 8\gamma_3' + 0.1255Z^2 \right], \\
2aC_{12} &= \frac{e^2}{V} \left[ -\frac{A}{3} + A_1 + A_2 - 6\gamma_1' - 4\gamma_2' - 4\gamma_3' - 1.3240Z^2 \right],
\end{align*}

and

\begin{equation}
2aC_{44} = \frac{e^2}{V} \left[ \frac{A}{3} + A_1 + A_2 + 2\gamma_1' + 4\gamma_2' + 8\gamma_3' - 0.0630Z^2 - \left( \frac{p_1^2}{p_2} \right) \right], \tag{2.37}
\end{equation}

where $Z$, being treated as disposable parameters, is calculated using the two zone-centre ($\Gamma$) phonon frequencies $\nu_{LO}(\Gamma)$ and $\nu_{TO}(\Gamma)$ given by

\begin{align*}
\mu\pi^2\nu_{LO}(\Gamma) &= \left( \frac{e^2}{V} \right) \left[ \frac{A_1}{3} + 8\gamma_1' + 8\gamma_2' + \left( \frac{2\pi}{6} \right)Z^2 \right], \tag{2.38a} \\
\mu\pi^2\nu_{TO}(\Gamma) &= \left( \frac{e^2}{V} \right) \left[ \frac{A_1}{3} + 8\gamma_1' + 8\gamma_2' - \left( \frac{\pi}{6} \right)Z^2 \right], \tag{2.38b}
\end{align*}

where \( p_1 = 1.2595Z^2 - 4\gamma_1' \)
and \[ P_2 = \left[ \frac{A_1}{3} + 8y'_1 + 8y'_2 - \left( \frac{\pi}{6} \right) Z^2 \right]. \]

Here \( a \) is the semilattice constant and \( \mu = \left( \frac{m_1m_2}{m_1 + m_2} \right) \) is the reduced mass.

### 2.6 EVALUATION OF MODEL PARAMETERS

Our TBSM model involved 11 parameters. These parameters are

\( A, A_1, A_2, \gamma_1, \gamma_2, \gamma_3, \alpha_1, \alpha_2, d_1, d_2 \) and \( Z' \).

<table>
<thead>
<tr>
<th>Nature of interaction</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Two-body</td>
<td>( A, A_1, A_2 )</td>
</tr>
<tr>
<td>(b) Three-body</td>
<td>( \gamma_1, \gamma_2, \gamma_3 )</td>
</tr>
</tbody>
</table>
| (c) Shell-model       | (i) Electronic polarizabilities \( \alpha_1 \) and \( \alpha_2 \)  
                        | (ii) distortion polarizabilities \( d_1 \) and \( d_2 \)  
                        | (iii) effective charge parameter \( Z' \) |

These parameters are calculated in the following expressions:

\[
A = \frac{3}{4} \frac{V}{e^2} \mu_{\omega_TO} \left[ \frac{\varepsilon_0 + 2 \varepsilon_\infty}{3 \varepsilon_\infty} \right]  \tag{2.39}
\]

\[
A_1 = \frac{1}{24} \left[ 3m_1 \omega_{LO}^2(X) - 4A - 6.495 \frac{(Ze)^2}{a^3} \right]  \tag{2.40}
\]

\[
A_2 = \frac{1}{24} \left[ 3m_2 \omega_{LA}^2(X) - 4A - 6.495 \frac{(Ze)^2}{a^3} \right]  \tag{2.41}
\]
\[ 2aC_{11} = \frac{e^2}{V} \left[ \frac{A}{3} + 2A_1 + 2A_2 + 12\gamma'_1 + 8\gamma'_2 + 8\gamma'_3 + 0.1255 Z^2 \right], \quad (2.42) \]

\[ 2aC_{12} = \frac{e^2}{V} \left[ -\frac{A}{3} + A_1 + A_2 - 6\gamma'_1 - 4\gamma'_2 - 4\gamma'_3 - 1.324 Z^2 \right], \quad (2.43) \]

\[ \mu \pi^2 v_{LO}(\Gamma) = \frac{e^2}{V} \left[ \frac{A_1}{3} + 8\gamma'_1 + 8\gamma'_2 + \left(\frac{2\pi}{6}\right) Z^2 \right], \quad (2.44) \]

\[ (Z'e)^2 = \frac{9}{4} \frac{V\mu\omega_{TO}^2(\Gamma)}{\pi} \frac{(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_\infty + 2)^2}, \quad (2.45) \]

\[ \alpha_2 = \frac{3V}{4\pi} \frac{(\varepsilon_\infty - 1)}{(\varepsilon_\infty + 2)}, \quad (2.46) \]

\[ \alpha_1 = \frac{3V}{4\pi} \left( \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} - \alpha_2 \right), \quad (2.47) \]

\[ d_1 - d_2 = Z' - Z, \quad (2.48) \]

\[ \frac{d_1}{d_2} = \frac{\alpha_1}{\alpha_2}. \quad (2.49) \]

2.7 MIXED CRYSTALS AND MODE BEHAVIOUR

A solid may be considered as an ordered or disordered system depending on whether its atomic arrangement is lattice or not, corresponding to the ideal crystalline and amorphous states, respectively. Mixed crystal may be regarded as solid solution in which the crystalline lattice topology is preserved but in which atomic spatial arrangement depends on the molar concentration of impurity in the host crystals. Thus, they may be considered a particular case of
disordered system marked by a close association with the dynamics of the perfect crystal but lacking translational periodicity.

From the point of view of lattice dynamics, the mixed crystals can be divided into three classes. One class the so called 'One-mode behaviour' in which at \( q = 0 \) phonon frequencies each of the modes (infrared and Raman active or both) vary continuously with concentration from one end member to that of the other and appear with approximately constant intensity. The other class exhibit the 'two-mode behaviour' in which two set of phonon frequencies occur at the frequencies close to that of end members, the intensity of each mode being approximately proportional to the concentration of each component. The third class of mode behaviour called 'partly two-mode behaviour' or 'intermediate one-two mode behaviour'. In this type two sets of phonons are observed only over certain composition range and one set of phonons over the remaining composition range. These three type of mode behaviour are shown in Fig. (2.7).

2.8 GREEN FUNCTION TECHNIQUE

We consider a zinc-blende lattice constituted by two interpenetrating sublattices numbered 1 and 2 and occupied by three types of atoms A, B and C in a way that corresponds to the situation in the mixed crystal \( \text{AB}_{1-x}\text{C}_x \). The sublattice 1 is occupied by atoms of type A and sublattice 2 is occupied by atoms of type B and C. If the occupancy of sublattice 2 is randomly distributed in such a way that the concentration of B is \((1-x)\) and that of C is \(x\), then the situation is of
Fig. 2.7 Schematic representation of compositional variation in mixed system (a) Two mode type (b) Partly two mode type (c) One mode type.
homogeneous mixed crystal. The Hamiltonian for such a system can be written as

$$H = \sum_{\alpha \ell k} \frac{\{P_{\alpha}(\ell k)\}^2}{2M_{\alpha}(\ell k)} C_{\alpha}(\ell k) + \frac{1}{2} \sum_{\alpha \beta} \phi_{\alpha \beta}(\ell k, \ell'k') u_{\alpha}(\ell) u_{\beta}(\ell') C_{\alpha}(\ell k) C_{\beta}(\ell'k')$$

(2.50)

where $\alpha, \beta$ are sublattices indices, $\ell$ and $\ell'$ are lattice sites, $k$ and $k'$ denote atomic types, $P$, $M$, $u$ and $\phi$ are respectively momenta, masses, displacements and force constants. The force constant $\phi_{\alpha \beta}(\ell k, \ell'k')$ are defined in the usual manner as second derivative of potential energy and $\phi_{\alpha \alpha}(\ell k, \ell k)$ is defined as

$$\phi_{\alpha \alpha}(\ell k, \ell k) = - \sum_{\beta k'} \phi_{\alpha \beta}(\ell k, \ell'k') C_{\beta}(\ell'k')$$

(2.51)

The prime on the summation sign implies that $\ell' \neq \ell$ when $\alpha = \beta$. The coefficient $C$ introduces randomness into the system and are defined by

$$C_{\alpha}(\ell k) = 1, \text{ if the } \ell^{th} \text{ site on sublattice is occupied by a } k \text{ type of atom.}$$

$$= 0, \text{ otherwise.}$$

It easily follows that $\{C_{\alpha}(\ell k)\}^2 = C_{\alpha}(\ell)$ and $C_{\alpha}(\ell k) C_{\alpha}(\ell'k') = \delta_{kk'} C_{\alpha}(\ell k)$

Since the same site can not be occupied by two atoms. The eigen frequencies of the system are determined by the poles of the displacement. The displacement Green’s function which we define in the usual notation

$$G_{\alpha \beta}(\ell k, \ell'k'; t) = C_{\alpha}(\ell k) C_{\beta}(\ell'k') <u_{\alpha}(\ell; t), u_{\beta}(\ell'; 0)>$$

(2.52)
Starting from the equation of motion for \( G_{\alpha\beta}(\ell k, \ell'k';t) \) one can then show that its frequency Fourier transform obeys the matrix equation

\[
\left| \omega^2 M - L \right| G = C
\]

(2.53)

where \( M, L, G \) and \( C \) are all matrices and \( L \), the new matrix is defined by

\[
L_{\alpha\beta}(\ell k, \ell'k') = \phi_{\alpha\beta}(\ell k, \ell'k') \delta_{\alpha\beta} \delta_{kk'} \delta_{\ell\ell'} + C_{\alpha}(\ell k) \phi_{\alpha\beta}(\ell k, \ell'k')
\]

(2.54)

Mean lattice Green function \( G_0 \) can be defined following Edward and Jones\(^{34} \) through the equation

\[
\left| \omega^2 M - \langle L \rangle \right| G_0 = \langle C \rangle
\]

(2.55)

where the brackets \( \langle \rangle \) indicates the averaging over all the different possible configuration of the random system. The setting \( L - \langle L \rangle = F \), the fluctuation of the actual force constant matrix from its configurationally averaged value we get,

\[
G = G_0 \langle C \rangle^{-1} C + G_0 \langle C \rangle^{-1} F G
\]

(2.56)

On taking the average on both sides and iterating, we arrive at the series

\[
\langle G \rangle = \langle G_0 \rangle + G_0 \langle C \rangle^{-1} \langle F G_0 \langle C \rangle^{-1} C \rangle
\]

(2.57)

\[
+ G_0 \langle C \rangle^{-1} \langle F G_0 \langle C \rangle^{-1} F G_0 \langle C \rangle^{-1} C \rangle + \ldots \]
The averaged Green's function depends only on the difference of spatial coordinates \( R_\alpha(\ell) - R_\beta(\ell') \), so that we can obtain its Fourier transform \( <G_{0\alpha\beta}(kk',q,w)> \). This in turn enables to reach the concept of phonons in the random system.

When equation (2.55) is written in terms of its matrix elements and Fourier transformed with respect to wave vector \( q \), we get

\[
\sum_{\mathbf{n}\mathbf{q}} \left| \omega^2 - M_\alpha(k) - \phi_{\alpha\alpha}(kk) \right| \delta_{\alpha\beta} \delta_{nk} - C_\alpha(k) \phi_{\alpha\beta}(kn,q) \\
G_{0\beta\beta}(nk',q,w) = C_\alpha(k') \delta_{\alpha\beta} \delta(kk')
\]

(2.58)

where \( C_\alpha(k) = <C_\alpha(\ell k)> = \) concentration of \( n \) type atoms on the \( \alpha \) sublattice and \( G_0(q,\omega) \) and \( \phi(q) \) are the Fourier transforms of \( <G_0(\ell,\ell')> \) and \( <\phi(\ell,\ell')> \) respectively. The poles of \( G_0 \) determine the phonon frequencies in the mean lattice approximation. From equation (2.58) it is observed that these frequencies in the mean lattice approximation. From equation (2.58) it is observed that these frequencies are the solutions of the equation

\[
|\omega^2 M_\alpha(k) - \phi_{\alpha\alpha}(kk) \delta_{\alpha\beta} \delta_{kk'} - C_\alpha(k) \phi_{\alpha\beta}(kk',q)| = 0
\]

(2.59)

In a mixed crystal of the type \( AB_{1-x}C_x \) we have

\[
C_1^A = 1, \quad C_2^B = (1-x) \quad \text{and} \quad C_2^C = x, \\
M_1^A = m_A, \quad M_2^B = \frac{m_B}{(1-x)} \quad \text{and} \quad M_2^C = \frac{m_C}{x}.
\]

Also

\[
\phi_{11}(q,11) = P, \quad \phi_{22}(q,22) = (1-x)P, \quad \phi_{22}(q,23) = xP, \\
\phi_{12}(q,12) = Q, \quad \phi_{12}(q,13) = Q \quad \text{and} \quad \phi_{22}(q,33) = P.
\]

(2.60)
where $P$ and $Q$ are each $3 \times 3$ matrices with zinc-blende structure and are given by

$$
P = \begin{bmatrix}
kk & kk & kk \\
xx & xy & xz \\
kk & kk & kk \\
yx & yy & yz \\
kk & kk & kk \\
zx & zy & zz
\end{bmatrix}
$$

and

$$
Q = \begin{bmatrix}
kk' & kk' & kk' \\
xx & xy & xz \\
kk' & kk' & kk' \\
yx & yy & yz \\
kk' & kk' & kk' \\
zx & zy & zz
\end{bmatrix}
$$

Substituting in equation (2.59), we get the dynamical matrix for the mixed system $AB_{1-x}C_x$, of the similar type as given by Kutty:\(^{35}\)

$$
\begin{vmatrix}
P - m_A \omega^2 & (1-x)Q & xQ \\
(1-x)Q^* & (1-x)^2 P - m_B \omega^2 & x(1-x)P \\
xQ^* & x(1-x)P^* & x^2 (P - m_C \omega^2)
\end{vmatrix} = 0
$$

(2.62)
whereas for the pure crystal AB, at \( x = 0 \), the dynamical matrix is,

\[
\begin{bmatrix}
p - m_A \omega^2 & Q \\
Q^* & p - m_B \omega^2
\end{bmatrix} = 0
\]  

(2.63)

and for the pure crystal AC, at \( x = 1 \), the dynamical matrix is given by

\[
\begin{bmatrix}
p - m_A \omega^2 & Q \\
Q^* & p - m_C \omega^2
\end{bmatrix} = 0
\]  

(2.64)

On analyzing the equation (2.62), we find that it exhibits one mode behaviour for all values of \( x \). This in general is not necessarily the case.

### 2.9 EFFECT OF NON-RANDOMNESS FOR TWO-MODE BEHAVIOUR

It is known that the phonon frequencies depend on the concentration and the fine structure of the AB and AC bands. To obtain these features, one must introduce in addition to the effect of B on the AC interaction and of C on the AB interaction, the interactions between B and C. To describe these interactions we have introduced a non-randomness parameter \( \lambda \) varying with the concentration called the mixing parameter. The effect of \( \lambda \) is to increase the chance of finding B or C ion next to a given B or C ion respectively. When \( \lambda \) is zero, the distribution of B and C is random depending on the concentration \( x \) only. So, we have the occupancy of sublattice 2 as non-randomly distributed in such a way that \((1-x)B\) atom will interact with \((1-x)B\) atom as well as \(x\lambda C\) atom, similarly the \(XC\) atom will interact with \(xC\) atom and \((1-x)\lambda B\) atom. Therefore, the dynamical matrix for the mixed system \(AB_{1-x}C_x\) will be given by,
\[
\begin{vmatrix}
P - m_A \omega^2 & (1 - x)Q & xQ \\
(1 - x)Q^* & (1 - x)(1 - x + x\lambda)P - m_B \omega^2 & x(1 - x)(1 - \lambda)P \\
xQ^* & x(1 - x)(1 - \lambda)P^* & x|x + (1 - x)\lambda||P - m_c \omega^2|
\end{vmatrix} = 0 \quad (2.65)
\]

This determinant gives two-mode behaviour (i.e. two sets of phonon frequencies are observed at frequencies close to those of end members) for composition range \(0 < x < 1\), and one-mode behaviour at exact \(x = 0\) and \(x = 1\), in agreement with the experimental facts.

However, in the case of infinite dilution of the mixed crystal \(AB_{1-x}C_x\), i.e., \(x = 0\) and \(x = 1\), we will get local and gap modes. According to Chang and Mitra\(^{36}\) the condition of local and gap mode is a necessary condition for the two-mode behaviour, otherwise, the system will display one-mode behaviour. The present model exhibits two-mode behaviour for the entire composition range \(0 < x < 1\), and for \(x = 0\) and \(x = 1\), it reduces to one-mode behaviour as observed physically.

If however, the non-randomness in the sublattice 2, of the mixed crystal system is absent, we say \(\lambda = 0\), this reduces the above matrix (2.64) to give only one-mode behaviour (equation (2.62)). The non-randomness parameter (\(\lambda\)) for a particular concentration in mixed \(AB_{1-x}C_x\) crystal system is determined by fitting to one of the transverse optical (TO) phonon frequency of the experimental two-mode behaviour of the mixed \(AB_{1-x}C_x\) crystal system.
2.10 DERIVATION OF MATRIX ELEMENTS

It has been observed that most of the semiconducting III–V and II–VI mixed crystal systems of the type \( AB_{1-x}C_x \), occur in zinc-blende structure\(^7,37\), the same as that of their present members AB and AC, so the P and Q (3×3) matrices in equation (2.61) for the end member compounds AB and AC, are derived from zinc-blende lattice type structure. The modified rigid-ion model incorporating an effective ionic charge in the long-range interaction and a short-range interaction upto second neighbours have been used to study the phonon dispersion, the elastic constants the frequency distribution and the specific heat of mixed crystal systems of the type \( AB_{1-x}C_x \).

The main features of the models are (i) long-range electrostatic interactions incorporating an effective ionic charge \((e Z_{\text{eff}})\) to include the effect of polarization which is determined using the Lyddane–Sachs–Teller relation\(^26\), (ii) short-range interactions including central and angular interaction between ions effective upto second neighbours, (iii) The force constants for the end member AC and BC, evaluated using the experimental values of the three elastic constants and two phonon frequencies, (iv) The force constants for the mixed system \( AB_{1-x}C_x \) determined assuming a linear variation with \( x \) from Vegard\(^37\).
2.11 FORCE CONSTANTS FOR THE MIXED SYSTEM

The force constants for the mixed $\text{AB}_{1-x}\text{C}_x$ are considered to vary linearly from one end member to that of the other following Vegard’s law

$$\alpha_{\text{AB}_{1-x}\text{C}_x} = \alpha_{\text{AB}}(1-x) + \alpha_{\text{AC}}(x) \quad (2.66)$$

where $x$ is the composition for $\text{AB}_{1-x}\text{C}_x$ mixed system.

A similar type of variation has been assumed for calculating the lattice constant the effective ionic charge and the dielectric constant for the mixed $\text{AB}_{1-x}\text{C}_x$ crystal system are given as follows:

$$a_{\text{AB}_{1-x}\text{C}_x} = a_{\text{AB}}(1-x) + a_{\text{AC}}(x) \quad (2.67)$$

$$Z_{\text{eff}} \text{AB}_{1-x}\text{C}_x = Z_{\text{eff}} \text{AB}(1-x) + Z_{\text{eff}} \text{AC}(x) \quad (2.68)$$

$$\varepsilon_{\text{in}} \text{AB}_{1-x}\text{C}_x = \varepsilon_{\text{in}} \text{AB}(1-x) + \varepsilon_{\text{in}} \text{AC}(x) \quad (2.69)$$
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