CHAPTER-III

DYNAMICAL MODELS FOR MIXED CRYSTALS

3.1 EXISTING MODELS FOR MIXED CRYSTALS

Although it is known that the mixed crystals generally have the same crystal structure as the parent crystals, the actual distribution of the constituent ions over the sublattices is not known. Lack of this information hinders one in proposing any microscopic theory to analyse the properties of mixed crystals. If certain assumptions were made on the distribution of the ions in the crystal lattice, then one may treat the mixed crystal problem in a similar manner as one treats the pure crystal. So to interpret the observed variation of frequency with composition in mixed crystals, a number of theoretical models and approximations have been proposed. A review of the experimental data as well as the models has been given by Chang and Mitra\(^1\), Barker and Sievers\(^2\) have made an extensive review of lattice vibrations associated with defects, emphasizing the infrared absorption and Raman scattering spectra. Some of the models normally employed for the study of mixed crystals, are discussed here with their merits and demerits. These theoretical models are described here below.

3.1.1 Virtual Crystal Approximation (VCA) Model

This is the simplest approach to describe the physical properties of the mixed crystals. Langer\(^3\) has obtained this virtual crystal approximation result in a case which is a one-dimensional chain of point masses connected to each other by springs. In the VCA, the mixed crystal is replaced by an equivalent ordered crystal with each lattice site occupied by the same type of hypothetical atom, whose masses are uniquely defined by the composition of the virtual crystal. Braunstein et al\(^4\) have found that the virtual crystal approximation predicts an essentially linear variation with composition for nearly all the modes, i.e. including zone-centre as well as zone boundary modes.
3.1.2 Pseudo-Unit-Cell Model

Chang and Mitra\textsuperscript{5,6}, beginning with the concept that the mixed-crystal behaviour must follow the pattern of the pure end-members, developed the concepts of the pseudounit-cell to explain the zone-centre phonons at any concentration. They assumed in a mixed crystal, $AB_{1-x}C_x$, that the mixing atoms are randomly distributed and that the components of the unit cell are defined as $A$, $(1-x)B$ and $xC$ (for $0 \leq x \leq 1$), where $B$ and $C$ are the substituting ions. The force on ion $A$ due to ion $B$ is given by $(1-x)F_{AB}$ due to ion $C$ by $xF_{AC}$, but the force exercised in $B$ due to $A$ is $F_{AB}$ and the one on $C$ due to $A$ is $F_{AC}$, because the molar fraction of ion $A$ is one. The generalised equations of motion in a one-dimensional mixed diatomic unit cell were proposed by Vetelino and Mitra\textsuperscript{7}. Varshney et al\textsuperscript{8} have calculated the lattice dynamics of $\text{ZnS}_{1-x}\text{Se}_x$ and $\text{GaP}_{1-x}\text{As}_x$ using the pseudo-unitecell model and coupling coefficients of the rigid-ion model of lattice dynamics affected by molar-concentration factors. Twelve constants are calculated from physical observables. However, to fill the gap between the experimental data and unknown input a fitting in the least-squares sense is introduced that results in an elaborate procedure with no immediate physical interpretation, this precluding the generalization of the method.

3.1.3 Linear Chain Model

Matossi\textsuperscript{9} has considered a linear diatomic chain model which considers only nearest-neighbour force constants to considers only nearest-neighbour force constants to discuss the one-mode behaviour of $\text{Na}_{1-x}\text{K}_x\text{Cl}$. One mode behaviour of mixed crystals, one really has to assume the absence of Clustering\textsuperscript{10,11}.

3.1.4 Random-Element Isodisplacement (REI) Model

Chen et al\textsuperscript{12} proposed their random-element isodisplacement model, which is based on the idea that the appearance of two resistrahlen bands may be thought,
of as consequence that the two mixing components in $AB_{1-x}C_x$ are in sublattices that vibrate rather independently against the lattice of the non mixing ion sub-lattice.

They assumed that the cation and anion of the like species from units that vibrate with the same phase and amplitude. The important factor in this model is that the force constants $F_{AB}$, $F_{AC}$ between ions A and B, and A and C, change linearly with concentration as do the lattice constants. However, the force constant $F_{BC}$ is a fitting parameter. A step forward had been achieved by Chang and Mitra by modifying the REI model (MREI) so that it includes the coulomb field. The result employing this field is that the model reproduces the known long-wavelength frequencies for any molar concentration, for two-mode and one-mode behaviour system. The striking feature of this model is that, using boundary conditions pertaining to the end members, it is possible to derive a criterion predicting the behaviour of mixed crystal. If the force constant do not change drastically with mixing ratio in a mixed crystal system, the criterion is expressed by an inequality $m_B < \mu_{AC}$, ($\mu$ is the reduced mass of A and C). Those mixed system which obey the inequality exhibit two-mode behaviour, whereas the opposite is true for one-mode system.

However, there are still some ambiguous cases which do not obey this inequality. Chang and Mitra have suspected that the condition of the local-gap mode is the necessary condition of the two-mode behaviour, Otherwise, the system will display onemode behaviour. The condition thus derived is latter suspected not to be a strong enough condition.

3.1.5 Coherent Potential Approximation (CPA) Model

The coherent potential approximation (CPA) of Taylor and Soven has been successfully applied by Taylor to a one-mode and a two-mode system. He could find qualitative agreement between calculation and experiment throughout the composition range. The coherent potential approximation is usually referred to as the self-consistent approach. The CPA yields a self-energy, which is invariant with
respect to the choice of the reference lattice. The criteria proposed by Elliott et al.\textsuperscript{16} based on coherent potential approximation, is a potentially use-full approach to study the mixed crystal systems. They have applied this approach to twenty eight mixed crystal systems successfully.

This method\textsuperscript{17} is especially applicable to concentrations 0.05<x<.95 (where cluster effects are important) and reduced to single defect theory as x→0 and (1-x)→0 due to the self consistent evaluation of the specially carying self energy.

3.2 GREEN'S FUNCTION TECHNIQUE

A more recent attempt to describe the lattice dynamics of mixed crystals of the type AB\textsubscript{1-x}C\textsubscript{x} was made by Kutty\textsuperscript{18} using the Green's function technique of Edward's and Jones\textsuperscript{19}. They considered a linear lattice constituted by two interpenetrating sublattices numbered “1” and “2”. The sublattice “1” is occupied by atoms of type A and the sublattice “2” is occupied randomaly by atoms of type B and C in such a way that the concentration of B is (1-x) and that of C is x, so that the situation of a homogeneous mixed crystal is obtained. In this case, the dynamical matrix thus formed gives three roots leading to one acoustic mode and two optic modes. In the limit x→0 two of these roots tend to the acoustic and optic modes of the host lattice, while the third mode becomes a flat localized mode or gap mode depending upon whether it falls above the optic band of the host or below. This behaviour is repeated when x→1 which, in general is not necessary the case.

The method, though theoretically sound, is quite cumbersome as it involves the use of complicated mathematics.

3.3 AN INTRODUCTION TO THE MODEL USED IN THE PRESENT WORK

In view of the above critical examination of some of the existing models, the modified random-element isodisplacement model of Chang and Mitra\textsuperscript{5} is
considered to be the most successful in predicting the behaviour of the mixed crystals. Even this formalism does not provide only two optical phonons at the zone-centre for pure crystals having two atoms per unit cell (it provides three) when reduced from the analysis of mixed crystals. Chang and Mitra have investigated that the appearance of local and gap modes is a necessary condition for the interpretation of two-mode behaviour. This does not appear to find experimental support.

3.4 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 regared as solid solution in which 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 in to 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 continously with concentration from one end member to that of the other and appear with approximately constant intensity. The other class exhibits 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" on 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(3.4).
Fig. 3.4 Schematic representation of compositional variation in mixed system (a) Two mode type (b) Partly two mode type (c) One mode type.
3.5 DERIVATION OF GREEN’S FUNCTION

We consider a Zinc-blende structure constituted by two interpenetrating sublattices “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 $AB_{1-x}C_x$. 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 a homogeneous mixed crystal. The Hamiltonian for such a crystal is written as

$$H = \sum \frac{\left\{P\left(\mathbf{l}\right)\right\}^2}{2M\left(\mathbf{l}\right)} C_{\alpha}\left(\mathbf{k}\right) + \frac{1}{2} \sum_{\alpha,\beta} \phi_{\alpha\beta}\left(\mathbf{l}\mathbf{k}', \mathbf{l}'\mathbf{k}\right) U_{\alpha}\left(\mathbf{l}\right) U_{\beta}\left(\mathbf{l}'\right) C_{\alpha}\left(\mathbf{l}\right) C_{\beta}\left(\mathbf{l}'\right)$$

(3.1)

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

$$\phi_{\alpha\alpha}\left(\mathbf{k}\mathbf{k}'\right) = - \sum_{\beta} \phi_{\alpha\beta}\left(\mathbf{l}\mathbf{k}', \mathbf{l}'\mathbf{k}\right) C_{\beta}\left(\mathbf{l}'\mathbf{k}'\right)$$

(3.2)

The coefficient $C$ introduces randomness into the system and are defined by

$$C_{\alpha}\left(\mathbf{l}\right) = 1 \quad \text{if}\ \text{ith site on sublattice is occupied by a type of atom},$$

$$C_{\alpha}\left(\mathbf{l}\right) = 0 \quad \text{otherwise}.$$

It easily follows that

$$\left\{C_{\alpha}\left(\mathbf{l}\right)\right\}^2 = C_{\alpha}\left(\mathbf{k}\right).$$

and

$$C_{\alpha}\left(\mathbf{l}\right) C_{\alpha}\left(\mathbf{l}'\mathbf{k}'\right) = \delta_{kk'} C_{\alpha}\left(\mathbf{l}\right)$$
since same site can not be occupied by two atoms. The eigen frequencies of
the system are determined by the poles of the displacement, the Green’s function
which we define in the usual notation.

\[ G_{\alpha\beta}(l\mathbf{k}, l'\mathbf{k}', t) = C_{\alpha}(l\mathbf{k})C_{\beta}(l'\mathbf{k}') \langle \langle \mathbf{u}_{\alpha}(l\mathbf{k}, t), \mathbf{u}_{\beta}(l'\mathbf{k}', 0) \rangle \rangle \]  \hspace{1cm} (3.3)

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

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

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

\[
\mathbf{L}_{\alpha\beta}(l\mathbf{k}, l'\mathbf{k}') = \phi_{\alpha\beta}(l\mathbf{k}, l'\mathbf{k}')\delta_{\alpha\beta}\delta_{l\mathbf{k}}\delta_{l'\mathbf{k}} + C_{\alpha}(l\mathbf{k})\phi_{\alpha\beta}(l\mathbf{k}, l'\mathbf{k}')
\]

Mean lattice Green function \( G_0 \) can be defined following Edward and Jones
through the equation.

\[
\left| \omega^2 \mathbf{M} - \langle \mathbf{L} \rangle \right| G_0 = \langle \mathbf{C} \rangle \]  \hspace{1cm} (3.5)

Where the brackets \( \langle \cdots \rangle \) indicates the averaging over all the different
possible configuration of the random system. Setting \( \mathbf{L} - \langle \mathbf{L} \rangle = \mathbf{F} \), the fluctuation
of the actual force constant matrix from its configurationally averaged value, we
get

\[
\mathbf{G} = G_0\langle \mathbf{C} \rangle^{-1}\mathbf{C} + G_0\langle \mathbf{C} \rangle^{-1}\mathbf{F}\mathbf{G} \]  \hspace{1cm} (3.6)

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

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

\[ \text{The averaged Green's function depends only on the difference of the special coordinates } |\mathbf{r}(1') - \mathbf{r}(1)|, \text{ so that we can obtain its Fourier transform } <G_{0,m}(kk'; \mathbf{q},w)> \text{. This in turn enables to reach the concept of phonons in the random system.} \]

When equation (3.5) is written in terms of its matrix elements and Fourier transformed with respect to wave vector \( \mathbf{q} \), we get

\[
\sum_{n,p} \left[ i\omega^3 M_{n} (k) - \phi_{nn}(kk)\delta_{\alpha\beta} \delta_{nk} - C(k)\phi_{\alpha\beta}(kn; \mathbf{q})\ G_{0\beta\beta}(nk; \mathbf{q},w) \right] = C_{a}(k')\delta_{\alpha\beta} \delta_{kk'} \quad (3.8)
\]

where \( C_{a}(k) = \langle C_{a}(k) \rangle \) is concentration of \( n \) type of atoms on the sublattice and \( G_{0}(\mathbf{q},\omega) \) and \( \phi(\mathbf{q}) \) are the Fourier transforms of \( <G_{0}(l,l')> \) and \( <\phi(l,l')> \) respectively. The poles of \( G_{0} \) determine the phonon frequencies in the mean lattice approximation. From equation (3.8) it is observed that these frequencies are the solutions of the equation

\[
\left[ i\omega^3 M_{\alpha} (k) - \phi_{\alpha\alpha}(kk,\mathbf{q})\delta_{\alpha\beta} \delta_{kk} - C_{a}(k)\phi_{\alpha\beta}(kk,\mathbf{q}) \right] = 0 \quad (3.9)
\]

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

\[
C_{1}^{A} = 1, \ C_{2}^{B} = 1-x, \text{ and } C_{2}^{C} = x,
\]

\[
M_{1}^{A} = m_{A}, M_{2}^{B} = \frac{m_{B}}{1-x} \text{ and } M_{2}^{C} = \frac{m_{C}}{x}
\]

Also

\[
\phi_{11}(q,l) = R, \ C_{22} (q,22) = (1-x)R, \ C_{22} (q,23) = xR
\]

\[
\phi_{12}(q,l) = S, \ C_{12} (q,13) = S \text{ and } C_{22} (q,33) = R
\]
where \( R \) and \( S \) are each \((3 \times 3)\) matrices with Zine-blende structure and are given by

\[
\begin{align*}
R &= \begin{bmatrix}
R_{xx}(q, 11) & R_{xy}(q, 11) & R_{xz}(q, 11) \\
R_{yx}(q, 11) & R_{yy}(q, 11) & R_{yz}(q, 11) \\
R_{zx}(q, 11) & R_{zy}(q, 11) & R_{zz}(q, 11)
\end{bmatrix} \\
S &= \begin{bmatrix}
R_{xx}(q, 12) & R_{xy}(q, 12) & R_{xz}(q, 12) \\
R_{yx}(q, 12) & R_{yy}(q, 12) & R_{yz}(q, 12) \\
R_{zx}(q, 12) & R_{zy}(q, 12) & R_{zz}(q, 12)
\end{bmatrix}
\end{align*}
\]

and substituting in equation (3.9), we get the secular determinant,

\[
\begin{vmatrix}
R - m_A \omega^2 & (1 - x)S & xS \\
(1 - x)S' & (1 - x)R - m_B \omega^2 & x(1 - x)R' \\
xS' & x(1 - x)R' & x^2(R - m_C \omega^2)
\end{vmatrix} = 0 \tag{3.10}
\]

For the pure crystal AB at \( x = 0 \), the above determinant

\[
\begin{vmatrix}
R - m_A \omega^2 & S \\
S' & R - m_B \omega^2
\end{vmatrix} = 0 \tag{3.11}
\]

For the pure crystal AC at \( x = 1 \), the secular determinant is given by

\[
\begin{vmatrix}
R - m_A \omega^2 & S \\
S' & R - m_C \omega^2
\end{vmatrix} = 0 \tag{3.12}
\]

On analysing the equation (3.10), we find that it exhibits one mode behaviour for all values of \( x \). This in general is not necessary the case.
3.6 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

$$
\begin{vmatrix}
R - m_A \omega^2 & (1-x)S \\
(1-x)S' & (1-x)(1-x+\lambda)R - m_B \omega^2 \\
xS' & x(1-x)(1-\lambda)R' \\
\end{vmatrix}
= 0 \quad (3.13)
$$

This determinant gives two-mode behaviour (i.e., two sets of phonon frequencies are observed at frequencies close to those of end member) 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 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\textsuperscript{20}, the condition of local and gap mode is necessary condition for the two-mode behaviour,
otherwise, the system will display one-mode display one-mode behaviour. The present model exhibits two-mode behaviour for the entire composition range 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 (equation 3.13) to give only one-mode behaviour equation 3.10).

The non-randomness parameter \( (\lambda) \) for a particular concentration in mixed \( \text{AB}_{1-x}\text{C}_x \) crystal system in determined by fitting to one of the transverse optical TO phonon frequency of the experimental two-mode behaviour of the mixed \( \text{AB}_{1-x}\text{C}_x \) crystal system.

### 3.7 DERIVATION OF MATRIX ELEMENTS

It has been observed that most of the semiconducting III-V and II-VI mixed crystal systems of the type \( \text{AB}_{1-x}\text{C}_x \), occur in Zinc-blende structure\(^{21,22} \), which is the same as systems AB and AC. So, the \( R \) and \( S \) (3x3) matrices for the end member compounds AB and AC, are derived from Zinc-blende lattice type structure. The modified Non-Central rigid-ion model (NCRIM) incorporating an effective ionic charge in the Coulombic range interaction and a non-Coulombic range interaction upto second neighbours have been used to study the phonon dispersion and the elastic constants, the frequency distribution and the specific heat of mixed crystal system of the type \( \text{AB}_{1-x}\text{C}_x \)

The main features of the model are

1. Coulombic electrostatic interaction incorporating an effective ionic charge (\( eZ_{\text{eff}} \) ) to include the effect of polarization which is determined using the Lyddane-Sachs-Teller relation\(^{23} \). (2) Non-Central interactions including central and angular interaction between ions effective upto second neighbours. (3) The
force constants for the end member AC and BC evaluated using the experimental values of the three elastic constants and two phonon frequencies. (4) The force constants for the mixed system $AB_{1-x}C_x$ determined assuming a linear variation with x from Vegard$^{21}$.

3.8 FORCE CONSTANTS FOR THE MIXED SYSTEM

The force constants for the mixed $AB_{1-x}C_x$ are considered to vary linearly from one end member to that of the other following Vegard’s$^{21}$ law

$$\alpha_{AB_{1-x}C_x} = \alpha_{AB}(1-x) + \alpha_{AC}(x)$$

(3.14)

where x is the composition for $AB_{1-x}C_x$ 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 $AB_{1-x}C_x$ crystal system are given as follows:

$$a_{AB_{1-x}C_x} = a_{AB}(1-x) + a_{AC}(x)$$

(3.15)

$$Z_{effAB_{1-x}C_x} = Z_{effAB}(1-x) + Z_{effAC}(x)$$

(3.16)

$$\varepsilon_{\infty AB_{1-x}C_x} = \varepsilon_{\infty AB}(1-x) + \varepsilon_{\infty AC}(x)$$

(3.17)
REFERENCES