

Chapter 2

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2.1

RELEVANT MODELS FOR SUPERIONIC SOLIDS

The superionic conductors sometimes called solid materials that display ionic conductivities that are typical of those found in molten salts. One of the simplest and best understood classes of superionic conductors consists of materials that crystallize in the fluorite structure. Superionic conductors have attracted a great deal of experimental and theoretical attention over the past few years, both because of their technology importance and because of their intrinsic scientific interest. On the other hand, the study of layer type crystal is important because of their experimental structural, optical and electrical properties. A particularly interesting class of such crystals is that of the transition metal dichalcogenide that crystallize in CdI_2 structure.

Now days, the superionic conductors are used as solid state batteries fuel cells, memory devices, display panels etc. Whereas the transition metal di- chalcogenides, present some interesting magnetic properties, some are today the object of numerous studied on metal insulator transition, charge density waves, superionic conductivities. Numerous applications of these materials have increased the need of knowing their lattice dynamical properties quantitatively.

Since Phonon, being one of the elementary excitations of solid provide important and unique information of the materials, the lattice dynamical studies of the mixed superionic crystals having fluorite structure and the mixed transition metal di-chalcogenide, having CdI_2 structure, have been carried out.

In present work , there for , phonon dispersion, frequency spectra, specific heats and elastic constant of some mixed super ionic crystals,

$\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$, $\text{Sr}_{1-x}\text{Cd}_x\text{F}_2$, $\text{Mn}_x\text{Cd}_{1-x}\text{F}_2$, $\text{Ba}_x\text{Sr}_{1-x}\text{F}_2$ and $\text{Sr}_x\text{Ca}_{1-x}\text{F}_2$ have been studied by using modified rigid ion model incorporating the presence of non central forces. Earlier Gupta et al^[52,53] studied such materials using Gazis and Wallis^[32] and De Launey^[78] type angular forces. A critical comparison of the results that come out from the above two type of angular forces has been made by Gupta et al^[52,53].

2.1.1 RIGID-ION MODEL (RIM)

The foundation for the study of lattice dynamics was laid by Born^[11]. This model was used by Lyddane and Herzfeld^[92] in their calculation on the vibration spectra of alkali halides. Kellermann^[67] made a detailed study of the lattice vibrations of NaCl structure on the basis of this model. He assumed that the ions are regarded as the rigid (or undeformable) and unpolarizable point ions or spherically rigid-ions (plus and minus) and they are prevented from collapsing under their mutual Coulomb attraction by the presence of short-range overlap repulsion. Hence this model is often called the rigid ion (or point ion) model.

When the lattice is distorted during vibrations, the ions get displaced and may be represented by dipoles placed at the perfect lattice sites. This causes a change in the lattice energy due to dipole-dipole interactions summed over all the lattice sites in the solid. Since this interaction is of long-range in character, it is difficult to truncate the summation at any point due to slow convergence. This difficulty was overcome by Kellermann using the technique of Lodin^[80] for the calculation of Madelung energy. According to the picture of RIM, the potential energy of

interaction of pair of ions separated by a distance $|\vec{r}| = |\vec{r}^0(I' K') - \vec{r}^0(IK)|$ in chapter 1 is given by

$$\begin{aligned}\phi_{kk'}(r) &= \phi_{kk'}^{(C)}(|\vec{r}|) + \phi_{kk'}^{(R)}(|\vec{r}|) \quad (2.1) \\ &= \frac{1}{2} \sum_{Ik} \sum_{I'K'} \frac{Z_k e Z_{k'} e}{|\vec{r}|} + \phi_{kk'}^{(R)}(|\vec{r}|)\end{aligned}$$

Where $\phi_{kk'}^{(C)}(\vec{r})$ is Coulombic-contribution of the potential energy and $\phi_{kk'}^{(R)}(\vec{r})$ is the short-range overlap repulsion contribution. The matrix elements correspondingly may be divided into Coulombic and short-range non-Coulombic parts. Here $Z_k e$ and $Z_{k'} e$ are the charges on K^{th} and K'^{th} ions respectively. Thus from equation (1.6)

$$\phi_{\alpha\beta}(Ik, I' K') = \phi_{\alpha\beta}^{(C)}(Ik, I' K') + \phi_{\alpha\beta}^{(R)}(Ik, I' K') \quad (2.2)$$

In view of (2.1) the matrix elements are

$$D_{\alpha\beta}(\vec{q}, kk') = D_{\alpha\beta}^{(C)}(\vec{q}, kk') + \phi_{\alpha\beta}^{(R)}(\vec{q}, kk') \quad (2.3)$$

From the definition of $\phi^{(C)}$ The Coulombic part may be written as

$$D_{\alpha\beta}^{(C)}(\vec{q}, kk') = Z_k e C_{\alpha\beta}(\vec{q}, kk') Z_{k'} e \quad (2.4a)$$

Where the elements of the Coulombic matrix $C(\vec{q})$ may be written as

$$C_{\alpha\beta}(\vec{q}, kk') = \frac{1}{\sqrt{m_k m_{k'}}} \sum_I \frac{\partial^2 |\vec{r}^0(I' K') - \vec{r}^0(IK)|^{-1}}{\partial u_\alpha(IK) \partial u_\beta(I' K')} \exp(i\vec{q} \cdot (\vec{r}^0(I' K') - \vec{r}^0(IK))) \quad (2.4b)$$

The expression for $D_{\alpha\beta}^{(R)}(\vec{q}, kk')$ will be of the general type defined by

$$D_{\alpha\beta}^{(R)}(\vec{q}, kk') = \frac{1}{\sqrt{m_k m_{k'}}} \sum_{I'} \phi_{\alpha\beta}^{(R)} \exp(i\vec{q} \cdot (\vec{r}^0(I' K') - \vec{r}^0(IK))) \quad (2.5)$$

$$= R_{\alpha\beta}(q, kk')$$

Thus the matrix $D(\vec{q})$ can be written as

$$D(\vec{q}) = (ZCZ + R) \quad (2.6)$$

Where Z is a $(3n \times 3n)$ diagonal matrix formed from the ionic charges with elements

$$Z_{\alpha\beta}(kk') = Z_k e \delta_{\alpha\beta} \delta_{kk'} \quad (2.7)$$

C and R are $(3n \times 3n)$ diagonal matrices corresponding to the Coulomb and short-range (SR) non-Coulombic parts respectively. In view of (1.12) the equation of motion for RIM is

$$\omega^2(q)U(\vec{q}) = (R + ZCZ)U \quad (2.8)$$

This is rather a simple equation and is merely the matrix formulation of Kellermann's theory. This leads to the following characteristic equation.

$$\left| (R + ZCZ) - \omega^2 I \right| = 0 \quad (2.9)$$

Which can be solved for the frequencies $\omega_j(\vec{q})$. The determinant given by (2.9) is of the order 6 of cubic diatomic crystals. Since the Coulombic interaction in (2.1) being long-range in nature is not feasible to evaluate the series (2.4b) directly. In fact it does not tend to a unique value as $\vec{q} = 0$, but to a value, which depends on the relative direction of \vec{q} and the electrical polarization associated with the mode concerned. Kellermann's^[67] technique for solving this convergence problem shall be discussed in Chapter 3.

The acoustical modes in long wavelength limit are directly related to the elastic constants of a solid. The calculations based on the rigid-ion

model lead to the Cauchy-relation, which provides equality between the elastic constant C_{12} and C_{44} . But experimental observations show that the two elastic constants are different and such a relation is not satisfied though the discrepancies in the case of all alkali halides except LiF are small.

The Cauchy-discrepancy ($C_{12} \neq C_{44}$) implies the existence of many-body forces arising either from anisotropy in the electron distribution or angle bending. The former effect was thoroughly investigated by Lowdin^[81-83] to solve the problems of Cohesion and elastic properties. From his studies Lowdin confirmed the existence of many-body interactions and Lundqvist^[87-91] incorporated such forces in the study of the lattice dynamics of the ionic crystals.

While considering the dielectric properties of the ionic crystals, we know that these give a close relation with the long wave optical vibrations but it is seen that the theoretical curves for optical branches show much variation with the experimental dispersion curves. Hence, the rigid-ion model fails in explaining the dielectrical behaviour of the crystals. As this model considers the ion to be rigid and unpolarizable, the high frequency (optical) dielectric constant ϵ_∞ must be equal to unity for all ionic crystals. Experimentally it is found to be incorrect, for example, the observed value ϵ_∞ for NaCl is 2.25.

Another defect of rigid-ion model is that the values of the longitudinal optical frequency ω_{LO} obtained by this theory and by LST (Lyddane-Sacks Teller) relation^[93].

$$\frac{\omega_{LO}}{\omega_{TO}} = \sqrt{\frac{\epsilon_0}{\epsilon_\infty}} \quad (2.10)$$

differ widely. In (2.10) ϵ_0 is low frequency (static dielectric constant)^[114,115].

Szigeti^[114,115] while discussing the dielectric properties of alkali halides obtained two important relations namely.

$$m\omega_{TO}^2 \left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \right) = \frac{6a}{K} \quad (2.11a)$$

And

$$\epsilon_0 - \epsilon_\infty = \frac{(\epsilon_0 + 2)^2 4\pi N e_s^{*2}}{9m\omega_{TO}^2} \quad (2.11b)$$

Where N is the number of ion pairs per unit volume, m is the reduced mass of an ion pair and K is the compressibility, e_s^* is Szigeti effective charge of well known Szigeti relation^[114,115] given by (2.11 b).

It is seen that experimental quantities fail to satisfy the relation (2.11 b). Szigeti^[114,115] suggested a replacement of K by the effective compressibility and e by the effective charge e_s^* ($= < e$) respectively. The ratio e_s^* / e is found to be less than unity, while X-ray diffraction studies show that ionic charges of the alkali halides (except LiF and NaF) are not much different from effective ionic charges. So Szigeti^[114,115] suggested that apart from the ionic and electronic polarization, there is some further polarization due to mutual distortions of neighboring ions owing to their overlap. The effect can be described in terms of the multipole moments charge in the overlap region. These dipoles are termed as the “distortion dipoles”.

2.1.2 MODIFIED RIGID-ION MODEL (MRIM)

This model was first proposed by Vetelino and Mitra^[123] and later on developed by their coworkers^[125-127] is essentially a rigid-ion model which incorporates (a) the short-range central and non-central interactions and (b) the long-range Coulomb interactions among ions of appropriate effective ionic charge which ensures a proper LO-TO mode splitting. The development of this model is thus based on the concept of Szigeti effective charge^[114,115]. The expressions for the crystal energy and secular equation corresponding to MRIM are almost the same as those given, respectively. By (2.1) and (2.6) except the difference in the definition of ionic charge (Ze) and the extension of short-range forces up to second and sometimes third neighbour ions.

The MRIM contains in all five parameters (i) An effective ionic charge Ze , (ii) non-central force (α, β) for first neighbour, (iii) central second neighbour force constant assuming same for cation-cation and anion interactions and (iv) central third neighbour force constant. These parameters are determined with the use of three elastic constants and two zone-centre optic mode frequencies.

The effective ionic charge in MRIM is given by

$$(Ze)^2 = \frac{mV_a}{4\pi} (\omega_{LO}^2(\Gamma) - \omega_{LO}^2(\Gamma)) \quad (2.12a)$$

$$(Ze)^2 = \frac{mV_a}{4\pi} \omega_{TO}^2(\Gamma) (\epsilon_0 - \epsilon_\infty) / \epsilon_\infty \quad (2.12b)$$

Where m is reduced mass and V_a is atomic volume.

It is interesting to note that the relations (2.12) are not very much different from the corresponding Szigeti relation^[114,115] if one uses $\epsilon_\infty = 1$.

Also, the values calculated for the effective ionic charges from (2.12) are not much different from the Sziget, effective charge for most of the crystals.

2.1.3 VIRTUAL CRYSTAL APPROXIMATION (VCA) MODEL

This is the simplest approach to describe the physical properties of the mixed crystals. Langer^[77] has obtained the virtual crystal approximation result in a case which is a one dimensional chain of point masses connected to each other by spring. 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^[15] 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 mode.

The VCA turns out to be suitable for describing one mode behaviour and cannot predict the different type of behaviour in mixed crystals.

2.1.4 PSEUDO- UNIT CELL MODEL

Chang and Mitra^[22,24] belonging with the concept that the mixed crystal behaviour must follow the pattern of the pure end members developed the concept of the pseudo unit cell to explain the zone centre phonon at any concentration. They assumed in an 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 ($0 \leq X \leq 1$) where B and C are the substituting ions. The force on ions A due to ion B is given by $(1-X)F_{AB}$ due to ion C by XF_{AC} , because the molar fraction of ion A is one.

The generalized equation of motion in a one dimensional mixed diatomic unit cell were proposed by Vetelino and Mitra^[124], Varshney et al^[119] have calculated the lattice dynamics of $\text{ZnS}_{1-x}\text{Se}_x$ and $\text{GaP}_{1-x}\text{As}_x$ using the pseudo unit cell model and coupling coefficient of the rigid ion model of lattice dynamics affected molar concentration factors. Twelve constant are calculated from physical observables. However to fill the gap between the experimental data and unknown input fitting in the least square sense is introduced, this results in an elaborate procedure with no immediate physical interpretation, thus precluding the generalization of the method.

2.1.5 LINEAR CHAIN MODEL

Matossi^[100] has considered a linear diatomic chain model which considers only nearest neighbor force constants to discuss the mode behaviour of $\text{Na}_{1-x}\text{K}_x\text{Cl}$. This model is idealized with a periodic regular linear distribution of A ion and B ion in $\text{A}_{1-x}\text{B}_xC$ system, whereas the true distribution is believed to be random. It deals with the case of 50-50 mixing ratio and considers only those frequencies of the different branches of the entire spectrum in which homologous points oscillate with equal phase. Later Langer et al^[76] extended this model to discuss the two mode behaviour in $\text{CdS}_{1-x}\text{Se}_x$.

However this is only one dimensional treatment of the three dimensional solid neglecting its actual crystal structure.

2.1.6 CLUSTER MODEL

Verleur and Barker^[121] considered a short range clustering to account for the two mode behaviour of mixed crystal $\text{GaP}_{1-x}\text{As}$. They assumed that the negative ions have tendency to cluster around positive ions within a range of no more than a micron or two. They took a positive

Ga ion sublattice to be perfect and considered five basic units of nearest neighbors ion around a Ga ion site, i.e. a positive Ga ion may have 4 As, 3As and 1P, 2As, 2P, 1As and 3P and 4P ions as nearest neighbors, and introduced a clustering parameter, to obtain the weighted fractional distribution of these five basic units in the crystals. This model requires large number of parameters to explain the particular behaviour in ternary mixed systems. However to explain the one mode behaviour of mixed crystals, one really has to assume the absence of clustering.

2.1.7 RANDOM ELEMENT ISODISPLACEMENT (REI) MODEL

Chen et al^[26] proposed their random element isodisplacement model, which is based on the idea that the appearance of two 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 sublattice. They assumed that the cation and anion of the like species from units that vibrates with the same phase and amplitude. The important factor in this model is that the force constants F_{AB} , F_{AC} between ion 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^[22] 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 a 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 $m_b < \mu_{AC}$ (μ is the reduced mass of A and C). Those mixed system which obeys 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^[22] have suspected that the condition of the local gap mode is the necessary condition of the two mode behaviour; otherwise the system will display one mode behaviour. The condition thus derived is later suspected not to be a strong enough condition.

2.1.8 COHERENT POTENTIAL APPROXIMATION (CPA)

MODEL

The coherent potential approximation (CPA) of Taylor^[116] and Soven^[112] has been successfully applied by Taylor^[117] to a one mode and two mode systems. 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^[43] based on coherent potential approximation, is a potentially useful approach to study the mixed crystal system. They have applied this approach to twenty eight mixed crystal system successfully.

This method^[13] is especially applicable to concentration $0.05 < x < 0.095$ where cluster effects are important and reduces to single defect theory as $x \rightarrow 0$ and $(1-x) \rightarrow 0$. But it (CPA) is a numerically cumbersome technique due to the self consistent evolution of the specially varying self energy.

2.1.9 GREEN'S FUNCTION TECHNIQUE

A more recent attempt to describe the lattice dynamics of mixed crystals of the type $AB_{1-x}C_x$ was made by Kutty^[75] using the Green's function technique of Edward's and Jones^[42]. 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 by randomly 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 the homogeneous mixed crystal is obtained. In this case, dynamical matrix thus formed gives three roots leading to one acoustic mode and two optic modes. In the limit $x \rightarrow 0$ 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 of depending upon whether it falls above the optic band of the host or below. This behaviour is repeated when $x \rightarrow 1$ which, in general is not necessary the case.

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

In view of the above critical examination of some of existing models, the modified random element isodisplacement model of Chang and Mitra^[22] 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^[22] 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.

2.1.10 THE MICROSCOPIC APPROACH

Recently Makur and Gosh^[96,97] studied fluoride using the microscopic approach using an energy expression for the assembly of polarizable ions in the harmonic approximation, potential energy for such a system is given by

$$\phi = \frac{1}{2} \sum_{ij} \frac{Z_i Z_j}{r_{ij}} - \sum \mu_i (E_i^m + E_i^\mu) + \sum \frac{\mu_i^c}{2\alpha_i} + \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \frac{1}{2} \sum \phi S_{nn}(r_{ij}) \quad (2.13)$$

Where $\mu_e = \mu_i^c + \mu_i^d$

Where μ_i^c and μ_i^d are the deformation dipole moment due to first order exchange interaction and the dipole moment due to second order exchange interaction respectively E_i^m and E_i^μ denoted the monopole dipole fields. The first term in the above equation gives monopole coulomb interaction between the ions. The third term is the Vander Waal's interaction. Fourth term gives the change in overlap interaction between neighbors.

2.2

2.2.1 ZONE CENTRE MODE BEHAVIOUR

Experimentally, through far-infrared and Raman spectroscopy, it has been observed that for the mixed crystals of the type $A_{1-x}B_xC$ or $AB_{1-x}C_x$, there are at least three type of composition variations of the transverse optical (TO) mode frequencies and the longitudinal (LO) mode frequencies as schematically shown in figure (3.1). In some ternary mixed system, in one case only, one set of long wavelength of phonons will be evident, characteristic of the resultant system at any molar concentration, and in the other case, an equally typical behaviour, two sets of frequencies appear, i.e., a longitudinal optical (LO) and a transverse optical (TO_1) mode associated with one end member compound and a longitudinal optical (LO_2) and a transverse optical (TO_2) mode corresponding to the other end member compound. These two behaviour types are known in literature as one mode and two mode behaviour respectively. In addition, there are ternary mixed systems, in which two sets of TO and LO mode frequencies are observed only over certain composition, referred to as partly two mode types or intermediate one-two mode behaviour.

Figure (2.1) illustrate the so called two mode behaviour. Example of this type, in present investigation, are the mixed crystals, having CdI_2 structure as SnS_xSe_{2-x} , $HfS_{2-x}Te_x$, $TiSe_{2-x}S_x$ (for $0 \leq X \leq 2$) and $Hf_xTi_{1-x}Se_2$ and $ZrxTi_{1-x}Se_2$ (for $0 \leq X \leq 1$). Figure (2.1 b) shows an intermediate one two mode behaviour, and figure (2.1 c) shows only one set of TO and LO mode frequencies varying linearly with composition from frequencies of one end member.

In all three type of mode behaviour, it is found that the impurity mode occur for $x \rightarrow 1$ approaching end member compounds. These can be

local modes or gap modes, dependent whether they occur above the optical bands or between the acoustical and optical bands or within a phonon band respectively. The band impurity modes may be difficult to observe by IR or Raman spectroscopy, especially if they occur in regions of high phonon density of states while local or gap modes show up sharp lines.

2.2.2 ONE-MODE BEHAVIOUR

In the lattice dynamics of superionic mixed crystals $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$, $\text{Sr}_{1-x}\text{Cd}_x\text{F}_2$, $\text{Mn}_x\text{Cd}_{1-x}\text{F}_2$, $\text{Ba}_x\text{Sr}_{1-x}\text{F}_2$ and $\text{Sr}_x\text{Ca}_{1-x}\text{F}_2$ for all composition ranges have been carried out using modified rigid ion model (MRIM) with an appropriate effective charge in the electrostatic interaction and up to third neighbor for the short range forces. The electrostatic contribution is derived on the lines of Kellermann^[66]. The short range contribution to the dynamical matrix is derived during both type of angular forces, one due to De Launey^[78] and the other due to Clark, Gazis and Wallis^[32]. The phonon dispersion spectra obtained by using the above two type of angular forces in different directions, for the end members are calculated and compared with the experimental results. For the mixed systems, the force constant is assumed to vary linearly from one end member to the other end member. The lattice constant of mixed system obey Vegard's law in the whole compositional range^[70].

Thus the phonon spectrum of the mixed system for the whole compositional range is plotted which gives only one set of optical phonon frequency i.e. one mode behaviour.

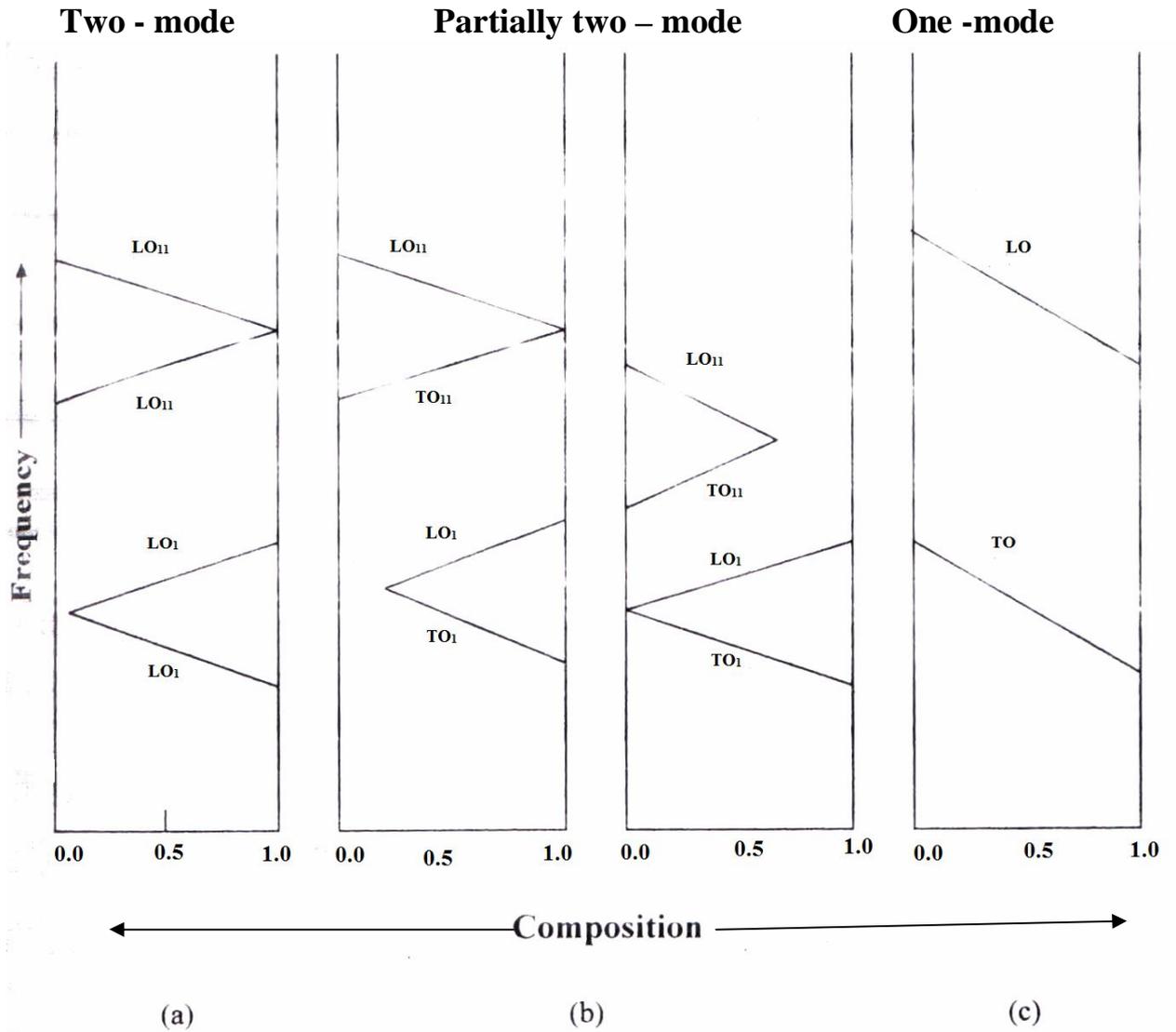


Figure 2.1 Schematic representation of the compositional variation in ternary mixed System (a) two mode type (b) partially two mode type and (c) one mode type.

2.2.3 TWO-MODE BEHAVIOUR

In the compositional dependent model has been proposed utilizing modified rigid ion model and introduces two coupling constants, λ_1 and λ_2 known as the intra layer and interlayer coupling constants, which explains the two mode behaviour of the mixed layered crystals $\text{SnS}_x\text{Se}_{1-x}$, $\text{HfS}_{2-x}\text{Te}_x$, $\text{TiSe}_{2-x}\text{S}_x$ (for $0 \leq X \leq 2$) and $\text{Hf}_x\text{Tl}_{1-x}\text{Se}_2$ and $\text{Zr}_x\text{Tl}_{1-x}\text{Se}_2$ (for $0 \leq X \leq 1$) see Gupta et al^[52,53].

Here it is considered that the unit cell of the mixed system $\text{SnS}_x\text{Se}_{2-x}$ (similarly in other mixed layered compounds having CdI_2 structure) spans only layer and contains only one molecular unit SnS_2 or SnSe_2 . Since SnS_2 and SnSe_2 are miscible in all proportion and form a complete range of binary solid solutions $\text{SnS}_x\text{Se}_{2-x}$ (for $0 \leq X \leq 2$) therefore it is expected that $(x/2)$ sulphur atoms will interact with $(x/2)$ sulphur atoms as well as with the $[(2-x)/2]$ λ_1 selenium atoms in a layer. Similarly $[(2-x)/2]$ selenium atoms interacts with the $(x/2)$ λ_1 sulphur atoms. The case for the coupling constant λ_2 is similar. Thus the dynamical matrix for the mixed system formed, will give two mode behaviours (four sets of optical phonon frequencies) for all values of x lying between $0 \leq X \leq 2$.

This two mode behaviour reduces to one mode behaviour (gives pure crystal behaviour) at the $\lambda_1 = \lambda_2 = 0$. Also at exact $x = 0$ and $x = 2$ the determinant gives only four optical phonon frequencies at the zone centre for pure end members, while Chang and Mitra^[22] have indicated that for three dimension crystal the condition of the local and gap mode becomes the necessary condition of the two mode behaviour. The present mode exhibit two mode behaviour for the entire composition range $0 \leq X \leq 2$ and for $x = 0$ and $x = 2$ reduces to the pure crystal behaviour.

2.3

FREQUENCY DISTRIBUTION FUNCTION OR PHONON DENSITY OF STATES

The frequency distribution function $g(\nu)$ of the normal modes of vibration of a solid is a key property from which various thermodynamic quantities can be calculated. The phonon wave vectors are uniformly and densely distributed in the Brillion zone. Since for each q there is a complete set of phonon frequencies, we can define a distribution of frequencies in each cement of volume in q space, and this can be regarded as continuous function of frequencies. The distribution function $g(\nu)$ is defined so that $g(\nu) d\nu$ is the number of frequencies lying between ν and $\nu + d\nu$.

Early investigation of the frequency distribution function as already mentioned were carried out by Blackman^[9] and Kellermann^[66]. Dayal and Tripathi^[37] have pointed out that there are some mistakes in the appropriated assignment of weights in the original formulation of Kellermann^[66]. This has been discussed in detail in Chapter 1. In the sampling method, one has to solve the dynamical matrix, obtained for the fluorite and CdI₂ structure, to generation a large number of frequency for a large number of uniformly distributed points (corresponding to different values of wave vectors) in the first Brillion zone and then to approximate the spectrum by a normalized histogram. To obtain the complete frequency distribution, the first Brillion Zone is divided into 1000 points (wave vector) and the secular determinant is solved. However, with appropriate assignment of weights^[54] to the frequencies corresponding to the points in the interior on the faces on the edges and at the corners of the first Brillion zone, the frequency distribution function can be calculated with reasonable

accuracy using 48 and 84 non equivalent points for the fluorite and CdI_2 structures respectively. These non equivalent points (wave vector) along with their appropriate weights for fluorite and CdI_2 structures have been given in tables **1.3** and **1.7** respectively.