Preface

Phonons, being one of the elementary excitations of solids provide important and unique information about mixed systems. But the complexity of the mathematical problems that arise in the study of lattice vibrations in disordered mixed system has resulted in a variety of approaches and approximations. Of all these attempts, the modified random-element-isodisplacement model of Chang and Mitra[21] is considered to be the most successful in predicting the behaviour of mixed crystals.

Fast ion conducting crystals, having CdI_2 structure are ionic materials with high electrical conductivity comparable with those of liquid electrolytes. These materials are also termed as, solid electrolytes or super ionic solids. Since the discovery of fast sodium ion conduction in β-alumina and silver ion conductivity in MAg_4I_5(M= K,Rb,NH4)[20], a large number of such solids have been discovered and numerous applications have been found ,such as solid batteries ,fuel cells, memory devices, display panels etc. On the other hand the layered crystals with CdI_2 (C_6) structure form an ample class of binary compounds. Several of them, metals present interesting magnetic properties; some are today the object of numerous studies on metal insulator transition charge density waves, super ionic conductivity[64,129]. Transition metal dihalides which still have a relatively large iconicity also show interesting and complex vibronic Features in the region of the crystal field transition. All these aspects, widely investigated in recent years have increased the need of knowing quantitatively the lattice dynamics of these crystals.

Vibrational, thermo dynamical, elastic, dielectric, optical, electrical, thermal and numerous of other physical properties depend on the motion of the constituent atoms (or ions) of the crystals. So knowledge of actual form of phonon frequency spectrum is required. Frequency spectrum can be achieved by means of theoretical models of lattice dynamics. Therefore in the present work we propose to study

phonon dispersion frequency spectra, specific heats and elastic constants of some mixed superionic crystals and transition metal dichalcogenides crystals by using modified rigid ion models incorporating the presence of angular forces, one due to Clark, Gazis and Wallis[32] (on the lines of Born[12]) and the other that of De. Launey[78]. A critical comparison of the results that come out from the above two types of angular forces has been made.

There are three types of compositional variations of the phonon frequencies

1. One mode behaviour for which one set of phonon frequency varies with the concentration of the components.
2. Two mode behaviour for which two sets of phonon frequencies are observed to occur at frequencies close to those of end members for all composition.
3. There are very few mixed crystals in which two sets of phonon frequencies are observed only over certain composition range and one set of phonon frequency over the remaining composition known as partly two mode type.

The mixed crystals studied.

1. Those showing one mode behaviour

   $Pb_xCd_{1-x}F_2$, $Sr_{1-x}Cd_xF_2$, $Mn_xCd_{1-x}F_2$, $Ba_xSr_{1-x}F_2$ and $Sr_xCa_{1-x}F_2$

2. Those showing two mode behaviours;

   $SnS_xSe_{1-}x$, $HfS2_{-x}Te_x$, $TiSe_{2-x}S_x$ (for $0 \leq X \leq 2$)

   and $Hf_xTi_{1-x}Se_2$ and $ZrxTi_{1-x}Se_2$((for $0 \leq X \leq$ l)

Theoretical investigations of the mixed crystals showing one mode behaviours are already made[132]. In present study we will study the mixed crystals showing two mode behaviours. Crystals for all composition ranges using the bond bending rigid ion model (BBRIM) with an appropriate effective charge in the electrostatic interaction. We have taken the interaction comprising short- range and

long-range Columbic. The short-range part is considered up to the third nearest neighbor. The electrostatic contribution is derived on the lines of Kellermann[66]. The short-range contribution to the dynamical matrix is derived using both the first order derivative as well as the second order derivative of the crystal potential energy. The valence force field method as developed by us for this purpose is used. The phonon dispersion relations, density of states, specific heats etc. are calculated for end members of mixed systems. We have compared our calculated results with available experimental optical data, for the mixed system, the force constants are assumed to vary linearly from one end member to other end member. The lattice constants of the mixed system obey Vegara's[70] law in the whole compositional range. 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. Valakh et al[118] and Kosacki et al[72] have discussed the lattice dynamics and superionic properties of $Pb_xCd_{1-x}F_2$ mixed crystals. They conclude that the interatomic force constants have almost no correlation with the ionic conductivity of super ionic mixed crystals. Makur et al[95] studied the dielectric properties and specific heat of superionic fluorites. Recently Sinha and Wakamura[109] explained the lattice dynamics of perovskite type superionic conductors.

Mixed crystals SnS_xSe_{2-x}, $HfS_{2-x}Te_x$, $TiSe_{2-x}S_x$ for $0 \leq x \leq 1$ belong to important class of materials called layered compounds showing two mode behaviour, in which the bonding with in the layers considerably stronger than the bonding perpendicular to it. Smith et al[111] have used the Keating type of bond bending force to investigate the Raman and infrared frequencies of SnX_2 compounds. In their calculations they restricted the bond bending forces to the Sn-S-Sn type only, omitting the X-Sn-S type of bond bending forces. In fact we found that the inclusion of S-Sn-S type of bond bending forces does not change the

frequencies at the zone centre but will change the phonon frequencies at the other points in all directions. Chanchal and Garg[17-19] also studied the two mode behaviour of mixed crystals by using Modified Random Element Isodisplacement Model (MREIM).

In the present work, a composition dependent model has been proposed utilizing modified rigid ion model with two coupling constants λ_1 and λ_2 which will explain the two mode behaviour of the mixed crystals of the type AB_XC_{2-X}($0 \leq X \leq 2$) with the local and gap modes occurring at $X \approx 0.0$ and $X \approx 2.0$ respectively whereas for exact X=0.0 and X=2.0 (for pure end members compounds). We have only four optical phonon frequencies as observed experimentally also.

The two mode behaviour reduces to one mode behaviour (gives pure crystal behaviour) at λ_1 and $\lambda_2 = 0$. Also at exact X = 0.0 and X = 2.0 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 dimensional crystals the condition of the local and gap mode becomes necessary condition of the two mode behaviour otherwise display one mode behaviour. The present model exhibit two mode behaviour for the entire composition range $0 \leq X \leq 2$.and for X = 0.0 and X = 2.0 it reduces to pure crystal behaviour.

In the present study, using the above mentioned model, two mode behaviour of the mixed layered crystals is established. Further a comparison of phonon dispersion of the mixed systems SnS_xSe_{2-x} $HfS_{2-x}Te_x$, $TiSe_2$-$_xS_x$ $Hf_xTi_{1-x}Se_2$ and $ZrxTi_{1-x}Se_2$ with experiment, are carried out using the model developed by us. The result calculated by using model developed by us in a good agreement with the available experimental data.

In chapter 1 we have obtained the secular determinant under harmonic approximation. We also discuss the structure of fluorites and CdI_2 lattice and their Brillouin zones and allowed wave vectors for calculating the phonon density of states.

In chapter 2 we discuss about theoretical models related to lattice dynamical studies of superionic solids. In this chapter we have given the multi-component mode behavior, i.e., one mode, two mode and partly two modes. Mixed crystals may be considered a particular case of disordered systems of the perfect crystal but lacking in the translational periodicity.

In chapter 3 we develop the bond bending rigid ion model. The potential energy is split in to short range and long range columbic parts. We have obtained matrix elements incorporating those interactions for superionic solids exhibiting multimode behaviour.

Chapter 4 describes the detailed study of superionic solids showing one mode behaviour. Results obtained by us have a satisfactory agreement with the experimental results.

In chapter 5 superionic crystals showing two mode behaviour are studied. We have introduced λ_1 and λ_2, interlayer and intralayer coupling constants for explaining the two mode behaviour in CdI_2 structure. Our results show overall good agreement with the experimental data.

The work which is included in the thesis is published in the form of the research papers listed below-

1 Lattice Dynamical Properties of $Sr_{1-x}Cd_xF_2$.

2 Lattice Dynamics of Superionic Crystal $Mn_xCd_{1-x}F_2$.