LATTICE DYNAMICAL STUDY OF MIXED CRYSTALS IN ROCK SALT STRUCTURE

By

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CERTIFICATE

We are satisfied that the thesis entitled "LATTICE DYNAMICAL STUDY OF MIXED CRYSTALS IN ROCK SALT STRUCTURE" by S. PRAKASH is worthy of consideration for the award of the Degree of DOCTOR OF PHILOSOPHY and is a record of the original bonafide research work carried out by him under our guidance and supervision. The results in it have not been submitted in part or full to any other university or institute for award of any Degree/Diploma.

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PREFACE

In the last decade, the study of lattice dynamics has experienced a resurgence in interest because of important developments in experimental techniques, viz.- the thermal neutron scattering, the laser excited Raman scattering, infra-red spectroscopy (reflection, transmission and emission experiments), edge emission and absorption, electron tunnelling effect and the refinements in x-ray technique. These enable one to obtain quite detailed and precise information on the lattice vibrations of solids which were largely unobtainable earlier from the study of thermal properties alone. Consequently, the whole field has become very much alive and substantial progress has been made in a period of few years.

At present, the semiconducting mixed crystals of the type $A_{1-x}B_xC$ and $AB_{1-x}C_x$ are being found to have more and more applications in modern technology. Out of these, the IV-VI semiconducting mixed crystals are favoured by well balanced metallurgy, the excellent uniformity in composition and the material stability at elevated temperatures. The band gap in such crystals (like $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$ etc.) varies with concentration x and can be narrowed down to any desired value by adjusting x. It is for this reason that such narrow band gap semiconducting mixed crystals are widely used in infra-red detection both as sensors of thermal radiation and as wide-band detector in the emerging areas of laser radar and laser communications. In addition to infra-red detectors and emitters, narrow band gap semiconducting mixed crystals have potential applications in the magneto-resistive, Hall-effect and thermoelectric devices. In view of the above, the theoretical study of such mixed crystals forms an important part of the present investigations.

The quest for the nature of interatomic interactions in solids is of paramount importance as it leads to an understanding of their vibrational, thermodynamical, elastic, dielectric, optical, electrical, thermal and neumerous other physical properties. All these properties depend on the motion of the constituent atoms (or ions) of the crystals and hence their study requires the knowledge of actual form of phonon frequency spectrum which can be achieved by means of theoretical models of lattice dynamics. In the present work, therefore, the phonon dispersions, frequency spectrum, specific heat and elastic constants of some selected mixed crystals on a modified rigid ion model suitable to such crystals have been studied.

In mixed crystal systems $A_{1-x}B_xC$, there are two different types of lattice vibrational behaviours. Crystals with a so called one-mode behaviour show only one longwavelength ($q \rightarrow 0$) transverse optical (TO) as well as one longitudinal optical(LO) phonon mode, their energy varying continuously with the composition x from the mode frequencies of the lighter component down to the mode frequencies of the heavier component. The other type exhibits two-mode behaviour. In this case, for an intermediate mixing ratio, two sets of phonon modes occur close to those of the end memers AC and BC. The oscillator strength of these modes are nearly proportional to the mole fraction of each component.

The selected mixed crystals are, therefore, divided into two categories :

1) Those showing one mode behaviour :

$Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$, $Ge_xSn_{1-x}Te$ and $K_{1-x}Rb_xCl$, $K_{1-x}Rb_xBr$, $Na_{1-x}K_xCl$ $KCl_{1-x}Br_x$, $KBr_{1-x}I_x$;

and

2) Those showing two mode behaviour :

$K_{1-x}Rb_xI$, $PbSe_{1-x}Te_x$

Limited efforts(1-8) have been made towards theoretical study of lattice dynamics of such mixed crystals. In some cases, the structure of mixed crystal is known, whereas in some other cases, it is not known and thus making their study more difficult. The most successful and recent is the Pseudo Unit Cell Model due to Chang and Mitra(1), which does not take into account the structure of the mixed crystal, but instead, assumes a Pseudo Unit Cell which is the repetitive unit to generate the whole crystal. Though the model gives qualitatively good results, it does not speak of the physics for the end-member crystals when the analysis is reduced from the two mode behaviour of the mixed crystals. In other cases, generally, the models used to study the pure binary compounds have been extended to study the lattice dynamics of mixed crystals. The models which can be physically applied to mixed crystals are modified rigid ion model[9] and Simple Shell Model[10] with some modifications. Out of these, the Shell Model was found to give good agreement with experimental results, but it involved a large number of fitting parameters, which when extended to ternary mixed crystals will involve still more parameters requiring correspondingly large number of experimental input data. In the absence of many experimental data for mixed crystals, the Shell Model, usually, can not be applied. However, very recently, Pirie & Ried[11] (1981) have also pointed out a serious flaw with Shell-Model calculations. Therefore, in the present investigations, a Modified Rigid Ion Model has been used.

In the present investigations, only those mixed crystals have been selected which occur in rock salt structure. The rock salt structure exhibits a high degree of ionicity because the coordination number of six for rock salt structure can not be reconciled with the directional valance bands. According to Philip's criterion (which applies strictly only to compounds having 8 valance electrons to the base) ionicity should exceed 0.785 for rock salt structure to occur. Hence Rigid Ion Model initially used by Kellermann[12] (1940) for NaCl should be a good model with proper modifications for compounds in rock salt structure. Since IV-VI semiconductors (like PbSe, PbTe etc.) have very high values of dielectric constant (i.e. large polarizabilities), the effect of large polarizability should be taken into account. Further as the IV-VI compounds are made up of heavy atoms with large core sizes, the interaction between ions/atoms should be considered effective upto larger number of neighbours. Hence here has been developed a Modified Rigid Ion Model to study the narrow band-gap IV-VI semiconducting mixed crystals in which the effect of large polarizability of atoms is incorporated by introducing an effective charge parameter (determined from L.S.T. relation) in the long range Coulombian contribution term. Also because of the large masses & large core sizes of the constituent atoms, the short range interaction has been considered effective upto four neighbors on the lines of de Launey[13]. The eight short range force constants (four central and four angular) for each of the end members (pure compounds) AC and BC in $A_{1-x}B_xC$ are first determined using three elastic constants and five phonon frequencies at the centre and at the boundary of first Brillouin Zone. The lattice constant, the effective charge parameter and the short range force constants for the mixed crystal are calculated assuming a linear variation with mixing concentration x.

STUDY OF CRYSTALS SHOWING ONE-MODE BEHAVIOUR :

Since the rock salt structure is two interpenetrating f.c.c. lattices, we assume here that for mixed crystal $A_{1-x}B_xC$, the atoms of type C occupy one f.c.c. lattice and the sites on second f.c.c. lattice are jointly occupied by (1-x)A and (x)B atoms forming a joint entity. We further assume a completely random distribution of these two types of atoms on their lattice. The problem is now treated similar to the case of pure binary crystals in the rock salt structure.

The theoretical calculations of phonon dispersions, elastic constants and specific heat are found to be in fairly good agreement with the available experimental results. The study of the above properties with varying mixing concentration x, has also been made. To test the general applicability of the model, it has also been applied to study some of the mixed alkali halide crystals in rock salt structure.

STUDY OF CRYSTALS SHOWING TWO-MODE BEHAVIOUR :

The two-mode behaviour exhibited by mixed crystals of the type $A_{1-x}B_xC$ is attributed to non-randomness in the distribution of the two types of atoms A & B on one of the f.c.c. sublattices. A non-randomness parameter β is introduced, which is evaluated by fitting to one zone centre frequency of the mixed crystal. Due to non-randomness in a mixed crystal $A_{1-x}B_xC$, (1-x)A atoms will interact with (1-x)A atoms as well as with $(x\beta)$B atoms. Similarly, xB atoms will interact with xB atoms as well as with $(1-x)\beta$ A atom. The dynamical matrix for evaluating the phonon frequencies is correspondingly modified, which now gives four optical phonons at the zone centre for some finite value of x. It is important to mention that the present model gives only two optical phonons at the zone centre for values of x = 0 and x = 1, the two extreme cases corresponding to the pure end-members AC and BC in agreement with the experimental facts; whereas, all the other existing models used by other workers in the field[1-8], give three optical phonons at the zone centre for exact values of x = 0 and x = 1, the third being referred to as local mode or gap mode as the case may be. The present model, however, gives local mode or gap mode in the cases of infinite dilution only i.e. when $x \approx 0$ and $x \approx 1$, but not at exact x = 0 and x = 1.

The phonon dispersions, elastic constants, frequency spectrum and specific heat have been calculated for various values of x for the selected mixed crystals. A fairly good agreement is found with available experimental results.

The work has resulted in the following research publications :

1. Phonon Dispersions in IV-VI Semiconducting Crystals
Nucl. Phys. Solid State Phys., India, C-24, 197(1981).
2. Phonon Dispersions in Narrow Band Gap Semiconducting Mixed Crystals.
J. Phys. Chem. Solids 44, 175(1983).
3. A Study of the Phonon Frequencies of Narrow Gap Semiconducting Mixed Crystal $Pb_{0.8}Sn_{0.2}Se$.
J. Chem. Phys. 75, 6335 (1983).
4. Thermal Properties of Narrow Band Gap Semiconducting Mixed Crystal $Ge_xSn_{1-x}Te$.
Phys. Rev.B, 27, 7636 (1983).
5. On Two-Mode Behaviour of Mixed Crystals.
Phys. Rev. B-28, 7390 (1983).
6. Effect of Non-Randomness on Long Wavelength Optical Phonons in $ZnS_{1-x}Se_x$.
Phys. Rev. B-28, 7191 (1983).
7. Effect of Mixing Concentration x on Thermal Properties of Mixed Crystal $K_{1-x}Rb_xBr$.
Nucl. Phys. & Solid State Physics, India C26 (1983).

CONTENTS

		Page No.
	PREFACE	(i)
	LIST OF PUBLICATIONS	(viii)
	REFERENCES	(ix)
CHAPTER I :	INTRODUCTION	1
	REFERENCES	15
CHAPTER II :	FORMULATION OF THE MODEL	19
	(a) CENTRAL OR RADIAL FORCES	25
	(b) ANGULAR FORCES	26
	EXPRESSIONS FOR ELASTIC CONSTANTS	31
	PHONON DISPERSION RELATIONS	32
	FREQUENCY DISTRIBUTION FUNCTION	34
	CALCULATION OF SPECIFIC HEAT AT CONSTANT VOLUME FOR VARIOUS TEMPERATURES	35
	REFERENCES	37
CHAPTER III :	MIXED CRYSTALS	38
	LATTICE DYNAMICS OF IV-VI NARROW-GAP SEMICONDUCTING MIXED CRYSTALS (SHOWING ONE-MODE BEHAVIOUR)	39
	$Pb_{1-x}Sn_xTe$	41
	$Pb_{1-x}Sn_xSe$	49
	$Ge_xSn_{1-x}Te$	53
	REFERENCES	61

CHAPTER IV : LATTICE DYNAMICS OF MIXED ALKALI HALIDES CRYSTALS (SHOWING ONE MODE BEHAVIOUR) 63

$K_{1-x}Rb_xBr$ 65

$KCl_{1-x}Br_x$ 73

$K_{1-x}Rb_xCl$ 78

$KBr_{1-x}I_x$ 81

$Na_{1-x}K_xCl$ 84

REFERENCES 88

CHAPTER V : THEORY OF TWO-MODE BEHAVIOUR 91

FORMULATION OF THE MODEL 92

REFERENCES 98

CHAPTER VI : LATTICE DYNAMICS OF MIXED CRYSTALS SHOWING TWO-MODE BEHAVIOUR 99

$K_{1-x}Rb_xI$ 104

$PbSe_{1-x}Te_x$ 110

REFERENCES 115

CONCLUSION : 116

(ENCLOSURES): REPRINTS OF PUBLISHED PAPERS