IPURITY-INDUCED LATTICE VIBRATIONAL MODES IN NON-METALLIC CRYSTALS

A. K. PRABHAKARAN

INDIAN INSTITUTE OF TECHNOLOGY, DELHI
1973

IMPURITY-INDUCED LATTICE VIBRATIONAL MODES IN NON-METALLIC CRYSTALS

A.K. PRABHAKARAN

Thesis submitted to
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
in partial fulfilment of the degree of
DOCTOR OF PHILOSOPHY

1973

ACKNOWLEDGMENTS

The author wishes to express his deep sense of gratitude to his esteemed guide and supervisor, Dr. K.P. Jain for his invaluable help, kind encouragement and constructive suggestions at various stages, without which the present work would not have been completed. The author also wishes to express his profound sense of gratitude to Prof. M.S. Sodha for his invaluable help and guidance.

The author is indebted to Dr. A.V.R. Warrier, now at Solid State Physics Laboratory, Delhi, for many valuable discussions he had with him on several occasions during the progress of this work.

The interest shown by Prof. K.L. Chopra and Prof. C.L. Mehta are also acknowledged.

The author is thankful to Prof. S.C. Jain and his group at Solid State Physics Laboratory, Delhi, for their encouragement and interest shown in this work.

The author is very grateful to Dr. S. Radhakrishna, now at Indian Institute of Technology, Madras, for the

help rendered by him in taking the Raman spectra of doped LiF crystals.

Dr. P.K.C. Pillai has always been an inspiration to the author. His encouragement and active help on several occasions are gratefully acknowledged.

Besides, in this academic achievement there were many personalities, whose keen interest and inspiration provided a favourable atmosphere to work. The help of many other colleagues in the department is also acknowledged.

Thanks are due to Mr. M.P. Joseph for his neat and accurate typing of the thesis.

Finally, the financial assistance given to this work by the Director, I.I.T. Delhi, and C.S.I.R., New Delhi, are gratefully acknowledged.

K. Parthasarathy.

THE PREFACE

Impurities in crystals produce many effects on the physical properties of crystals and a variety of experimental techniques have been used to study them. These effects include the appearance of new electronic levels in the forbidden gap, due to which new electronic absorption peaks are observed in the spectrum. Electrical and thermal conductivities are modified. Changes in thermal conductivity are observed as a dip in the curve due to resonant modes of impurities in a temperature range at which these modes are excited. The lattice vibration spectrum also changes. Additional modes like resonant, localised or gap modes appear depending on the nature of the impurity and the impurity-lattice interaction. So also the bulk thermodynamic properties are affected; for instance, the lattice heat capacity increases due to the resonant modes.

The appearance of resonant, localised or gap modes is an effect, which can be studied directly from a knowledge of the frequency spectrum of the host crystal. Resonant modes are impurity-modes introduced into the frequency spectrum of a crystal due to heavy impurities. These fall within the allowed frequencies of the host lattice spectrum.

Localised and gap modes fall outside the band of frequencies and the frequency gap between the acoustic and optic branches respectively. The first theoretical prediction of a localised mode in the case of a simple cubic crystal, was made by Lifshitz[1] in 1956. His work was later developed for real crystal structures by Dawber and Elliott[2], who derived expressions for the impurity-induced lattice vibrational modes in simple cubic, diamond and zinc-blende lattices. The first experimental evidence for a localised mode came in 1960 when Schaefer[3] observed a U-center local mode in KBr crystals. Since then much theoretical and experimental work has been done on impurity phonon-modes. In recent years, a wealth of experimental data on impurity modes in non-metallic crystals has appeared in the literature. This has stimulated theoretical work. Further, infra-red and Raman scattering experiments have been carried out in our Laboratory by Radhakrishna[4] and Jain et al.[5]. This has motivated and encouraged us to undertake the work reported in this thesis. It is hoped that it would contribute towards a better understanding of the impurity-lattice interactions in alkali halides, semiconductors like III-V compounds and group four elements.

In this thesis a simple theoretical model has been built up, using a model density of unperturbed phonon states[6],

to study the impurity-induced lattice vibrational modes in crystals. The general theory was originally given by Lifshitz[1] and subsequently developed by Dawber and Elliott[2] for localised modes in all real crystal structures. The possibility of quasi-localised or resonant modes was first discussed by Brout and Visscher[7]. This thesis focusses attention on the following aspects of the problem.

(i) The resonant modes of Ag^+ and Au^+ impurities in sodium halides have been calculated[6] in the mass defect approximation (MDA) of Brout and Visscher, which neglects changes in the force-constant due to the introduction of the impurity. As the MDA is inadequate for treating Ag^+ and Au^+ resonances in potassium halides, an estimate of the mode frequencies of these impurities should include force-constant changes. This has been done using a model due to Sievers and Takeno[8].

(ii) The MDA of Dawber and Elliott[2] has been applied to a treatment of localised modes due to light impurities in GaAs and GaP[9], with the model $\nu(\omega)$. The force-constant changes at the impurity sites in these crystals have also been estimated[9] using the Sievers and Takeno model. These results have been compared to a calculation of the force-constant changes on the molecular model[10].

(iii) Localised modes in silicon and germanium have been treated using a density of states calculated by Johnson[11] and Dolling and Cowley[12] respectively. The force-constant changes due to these impurities have also been estimated. This leads to a force-constant softening of 10 to 15% for these impurities.

(iv) Force-constant changes due to impurities in various crystals have been determined on the basis of either the band model[9] or the molecular model[10]. This has been done by fitting the simple theoretical models to experimentally observed mode frequencies. The results obtained in this fashion do not fall into a simple pattern, which would form the basis of an ab initio theory of force-constant changes.

The following is the chapter-wise summary of the work reported in this thesis.

The first chapter deals with a general introduction and the experimental background of the problem. Different theoretical models which attempt to treat the impurity modes are briefly reviewed here.

The second chapter discusses in detail, the general theory of phonon modes due to impurities in crystals. This

chapter describes the band model density of states for the phonons of the host lattice. The salient features of the model density of states are dealt with in considerable detail. Finally an outline of the different force-constant models for treating the problem are also given.

In chapter three, the theory of resonant modes due to Brout and Visscher has been used to study Ag^+ and Au^+ resonances in sodium and potassium halides. Ag^+ and Au^+ resonances in sodium halides can be described within the mass defect approximation (MDA). The MDA does not give any resonance in the low frequency acoustic region for Ag^+ impurity in potassium halides. Therefore Ag^+ and Au^+ resonances in potassium halides have been treated using a model which incorporates force-constant changes at the impurity sites[8]. This and a calculation of force-constant changes due to these impurities using the molecular model are also discussed here. A typical Raman scattering experiment is described in this chapter. The system chosen for study is Mn^{++} in LiF. Comparison of computed and observed resonant mode frequencies is made.

Chapter four discusses a calculation of localised modes in GaAs and GaP with the model density of states. The results in the MDA are compared with experiments.

The force-constant changes at the impurity sites calculated on the band model are compared to a calculation of these changes made on the molecular model.

In chapter five, the localised modes due to impurities in silicon and germanium are calculated using a density of states calculated by Johnson[11] and Dolling and Cowley[12]. The force-constant changes at the impurity sites are also calculated using the force-constant models[13]. This together with a general discussion of the effects of force-constant changes at impurity sites, concludes this chapter.

Lastly, chapter six summarises and evaluates the work. This also briefly discusses scope for further work in this field.

The work presented here has resulted in the following publications:

1. Raman scattering studies in LiF crystals containing manganese. Phys. Rev. B5, 2325 (1972).
2. Resonant phonon modes of Ag^+ and Au^+ in alkali halides. Phys. Rev. B6, 596 (1972).
3. Resonant phonon modes of Ag^+ in potassium halides. Phys. Letters 40A, 61 (1972).
4. Force-constant changes due to impurities in GaAs and GaP. Phys. Rev. B8, 1503 (1973).

5. Force-constant changes due to impurities in Si and Ge, submitted to Phys. Letters, 1973.

The following points of conclusion have been drawn from this work.

(i) For lighter alkali halides the MDA gives a good answer for impurity states; for instance Ag^+ and Au^+ resonances in sodium halides and Mn^{++} in LiF. But for heavier alkali halides, the MDA is inadequate and changes in force-constants at the impurity sites must be incorporated into the theory. When this is done good agreement is obtained with experiments; for instance, Ag^+ and Au^+ resonances in potassium halides.

(ii) The localised modes in III-V semiconducting compounds are determined chiefly by the analytic features of the density of states in the respective branches, rather than the details of the lattice dynamics or the details of the phonon spectrum of the host lattice.

(iii) The band model is more appropriate than a molecular model for treating force-constant changes at the impurity sites in GaAs and GaP. The molecular model is successful in yielding satisfactory results for force-constant changes due to impurities in alkali halides,(e.g. U- and F-centers). This is due to the assumptions involved in the model, that

in the case in alkali halides the localised modes are highly localised and it is possible to neglect all motions except that of the defect itself. For polar semiconductors like III-V compounds, and Group IV elements, the situation is different. Here the degree of localisation is much less, so that a molecular model becomes inadequate.

(iv) The force-constant changes for light and heavy impurities in different crystals, determined using the band and molecular models, do not fall into a recognisable pattern. It is, therefore, difficult to draw definite conclusions from the values obtained.

(v) This theory is unsuitable for very light impurities such as Li isotopes in GaAs and B isotopes in GaP. Calculation of mode frequencies of these impurities gives results in agreement with previous theoretical calculations, but differ considerably with the experiments. So it is pointed out that the present theories are inadequate for a satisfactory treatment of the modes of these impurities.

CONTENTS

	ACKNOWLEDGMENTS		i
	PREFACE		1
CHAPTER I	INTRODUCTION		
	1.1	General Background and the Experimental Situation	10
	1.2	Theoretical Background	13
		References	21
II	THEORY OF IMPURITY MODES AND THE DENSITY OF PHONON STATES		
	2.1	Introduction	24
	2.2	General Theory of Localised, Gap and Resonant Modes	24
	2.3	Singularities in the Frequency Spectrum	28
	2.4	Band Model Density of Phonon States	31
	2.5	Force-constant Models	33
		References	40
III	RESONANT PHONON MODES OF IMPURITIES IN ALKALI HALIDES		
	3.1	Introduction	41
	3.2	Resonant Modes of Ag^+ and Au^+ in Alkali Halides: Mass Defect Approximation (MDA)	42
	3.3	Ag^+ and Au^+ Resonances in Potassium Halides: Force-constant Model	50

3.4 Force-constant Changes: Molecular Model 55

3.5 Raman Scattering Studies of LiF Crystals Containing Manganese 59

3.6 Calculation of Resonant Mode Frequencies of Mn^{++} in LiF (MDA) 60

References 63

IV LOCALISED PHONON MODES DUE TO IMPURITIES IN ZINC-BLENDE TYPE LATTICES

4.1 Introduction 64

4.2 Localised Modes in GaAs and GaP (MDA) 65

4.3 Force-constant Changes Due to Impurities in GaAs and GaP: Band Model 71

4.4 Calculation of the Force-constant Ratio: Molecular Model 73

References 79

V LOCALISED PHONON MODES DUE TO IMPURITIES IN DIAMOND LATTICES

5.1 Introduction 80

5.2 Localised Modes in Si and Ge (MDA) 81

5.3 Force-constant Changes Due to Impurities in Si and Ge: Band Model 82

5.4 Force-constant Changes: Molecular Model 82

5.5 General Discussion of Force-constant Changes at Impurity Sites 86

References 89

VI SUMMARY, EVALUATION AND RECOMMENDATIONS

6.1 Introduction 90

6.2 Resonant Modes of Ag^+ and Au^+ in Alkali Halides 92

6.3 Localised Modes in GaAs and GaP: Band Model 97

6.4 Localised Modes Due to Impurities in Si and Ge 100

6.5 Force-constant Changes Due to Impurities 101

6.6 Summary 103

6.7 Scope for Further Work 105

References 107