LATTICE DYNAMICS OF GRAPHITE, ITS INTERCALATION COMPOUNDS AND ALKALI HALIDES

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TO

MY GRAND PARENTS

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(R.S. Narayanan)

PREFACE

The theoretical and experimental study of lattice dynamics of solids has been of great interest to physicists as it now forms an important part of any course in solid state physics. The vibrations of the constituent atoms at lattice sites play a significant role in determining the elastic, electrical, magnetic and thermal properties of solids. The vibrations also govern phenomena like diffuse scattering of x-rays, neutron scattering, spin lattice relaxation etc.

The present thesis has been devoted to the study of a newly developing group of compounds, viz graphite and its intercalation compounds, which comprises the first section. In the second part a study has been attempted on the alkali halides family based on a new quantum mechanical approach.

Graphite is a very good example of an element having layered structure[1]. The key property of layered structures is their anisotropy, making them suitable for a wide range of applications. An added feature of such compounds is their quasi two dimensional character that can be strengthened or weakened by intercalation with organic acids or metals respectively.

Graphite has a hexagonal layered structure with the layers tending to form weakly coupled hexagonal planar sheets[2]. The lattice belongs to the point group D^4_{6h}[3], with the unit cell containing four atoms. The forces between adjacent basal planes are nearly two orders of magnitude less than those between neighbouring atoms in the same plane[4]. Along the c-axis, the bonding is of the van der Waals type and very weak[5].

The earlier studies in graphite have been revolving around the Born-von Karman model[2,4,6-8]. However, deficiencies were observed while explaining the phonon spectrum or specific heat data. More recently, experimental studies have revealed for the first time, the occurence of a Raman active A_{2u} mode at 868 cm^{-1}[9]. Nemanich and Solin[10] pointed out that the key features of the phonon spectrum in graphite could be best explained only on the lines of Nicklow et al[4], but even that predicted the A_{2u} mode at $\approx$ 1400 cm^{-1} instead of at 868 cm^{-1}[11].

An attempt was made to explain this mode by Maeda et al[12] and Al-Jishi and Dresselhaus[13]. In both these models, the A_{2u} mode itself was taken as input data for determination of force constants etc., which in a way makes the force constants biased towards the experimental frequencies.

In the present work, the A_{2u} mode at 868 cm^{-1} has been explained satisfactorily without taking it as an input parameter and by using a lesser number of force constants, by employing an angular force model on the lines of deLauney[14].

In the present analysis interactions upto two neighbours in the basal plane and the nearest neighbour along the c-axis have been considered. While both the central and angular force constants have been employed for the nearest neighbours along the plane and along c-axis, only the central force constant has been employed for the second neighbour along the basal plane. Further, the five force constants thus used, are reduced to four by using the relation $\alpha_1=5\alpha_1'$ where α_1, α_1' are respectively, the first neighbour central and non-central force constants.

Though in the structure of graphite, only the alternate layers along the c-axis are identical as far as the position of carbon atoms in a hexagon are concerned, the present approach assumes all layers as identical, which is observed to occur upon intercalation[15]. Thereby, the in-plane force constants of graphite could be extended to the intercalation compounds[16]. The symmetry along c-axis facilitates the usage of the sum and difference mode analysis[17] in the present approach to solve the dynamical matrix.

Expanding the dynamical matrix in the long wavelength limit the expressions for the elastic constants C_{11}, C_{33} and C_{44} are obtained which are taken as input data together with the E_{1u} mode at 1575 cm^{-1}. The A_{2u} mode is observed at 909 cm^{-1} and the other branches in the phonon spectrum also indicate a good agreement with the available experimental results, though the quadratic nature of the transverse acoustic branch in the (qoo) direction at $q \rightarrow o$ is not observed in the present study.

The study of the graphite intercalation compounds, is primarily based on the stacking sequence employed along the c-axis which in turn, depends on the stage of the compounds. The stage, being the number of carbon layers between two intercalant layers i.e. a c-axis ordering is seen[18].

There have been only a few theoretical approaches to study these compounds[16,19,20], the variation in these approaches being due to the different stacking sequences adopted. But in these models, the number of force constant employed are large and the force constants have been obtained by fitting to experimental frequencies, with the basal plane force constants being extended from graphite which tends to make the model more dependent on experimental phonon frequencies.

In the present work, the first, second and the third stage graphite - alkali metal intercalation compounds have been studied. A stacking sequence of $C\alpha C\alpha C\alpha$..., $CC\alpha CC\alpha$..., $CCC\alpha CCC\alpha$.... respectively have been adopted for the first, second and the third stage compounds; where C,α denote respectively the carbon and intercalate layers. Along with the force constants obtained in graphite, additional central and non-central force constants have been employed to account for the carbon-metal interaction on the lines of Horie et al[16]. The dynamical matrix obtained is solved to get the phonon dispersion relations in the (qoo) and (ooq) directions, comparison with the available experimental results indicate a fairly good agreement.

Expansion of the dynamical matrix in the long wavelength limit yields elastic constants C_{33} and C_{44}. While the agreement in the case of C_{44} is satisfactory, when compared with the available experimental values, those for C_{33} are only qualitative.

The second part of the present study is devoted to the thermal properties of alkali halides. The various phenomenological models based on the principles in classical theory applied to the alkali halides have been numerous, starting from the earliest Born and von Karman theory[21] though the shell model[22], deformation dipole model[23] upto the modified rigid ion model [24,25] which was based on the rigid ion model developed by Kellermann[26,27].

In the present work, a newly developed form of overlap potential based on the first principles of quantum mechanics has been employed to study the alkali halides family. The ionic alkali halides family are widely used to test the validity of the interaction potential used, with special attention being paid to the phonon spectrum thus obtained, whose knowledge, helps gain insight into various properties[28].

In the present study, the quantum mechanical model that has been adopted is based on the tight binding theory developed by Harrison[29], wherein the Madelung term has been replaced by the band energy and the Born Mayer term by a quantum mechanical potential. Deviations are seen in the results obtained by

Harrison[29], which could probably be due to the replacement of the Madelung term by a band energy.

The present formulism while retaining the Madelung term, adopts a quantum mechanical overlap potential instead of the Born Mayer term on the lines of Harrison. The total potential energy will be the sum of the contributions from anion-anion, anion-cation and cation-cation interactions together with the Madelung term. The separation energies have been studied on the above lines and comparison with experimental results[30] is seen to indicate a good agreement.

The pressure derivative of bulk modulus has been evaluated and the results obtained in the present study are found to be in confirmity with those obtained experimentally[31-33], and those got by other workers based on the classical theory[34].

The phonon dispersion relations have been studied using an electrostatic contribution on the lines of Kellermann[26], by including an effective charge[35] to take into account the polarisability of ions and a short range overlap interaction effective upto the second neighbour within the framework of the modified rigid ion model[24], employing thus only four force constants - α_1, α_2 the central force constants for the first and second neighbour and α_1', α_2' the non central component. The dynamical matrix elements have been expanded in the long wavelength limit to give the elastic constants C_{11}, C_{12} and C_{44}.

The results indicate a satisfactory agreement in the dispersion relations when compared with the results obtained experimentally and those got by Karo and Hardy[36] based on the rigid ion model. The shear elastic constant C_{44} is also seen to exhibit a fair degree of agreement when compared with the experimental values.

The present thesis has been divided into two parts. The first part is devoted to the study of graphite and its intercalation compounds. Starting from the structure, the study traces the various approaches adopted to study graphite and its compounds with lithium, potassium, rubidium, and cesium for the stages one, two and three. It also describes in depth the present formulism to study graphite and its intercalation compounds.

The second part of the thesis is devoted to study the alkali halides family. The earlier models that have been employed to study the lattice dynamical properties have been cited. The Harrison's potential, a modified form of which has been used in the present study has also been described. The results obtained for the properties like binding energy, pressure derivative of bulk modulus, phonon dispersion and shear elastic constant have been discussed.

The entire work has been summed up in four chapters. The chapterwise summary is given below:

Chapter one deals with the lattice dynamics of graphite; starting from the structure of graphite, the chapter reviews the earlier work done and gives in detail the present analysis for the phonon dispersion and elastic constants of graphite. An appendix has been given on the deLauney's angular force model.

Chapter two deals with the graphite intercalation compounds, their structure and the various stages. Apart from the earlier studies undertaken, it gives an account of the formulism adopted in the present study to individually deal with the phonon dispersion relations and elastic constants for the first, second, and the third stages of the grahite-alkali metal intercalation compounds.

Chapter three is mainly for the review of the alkali halide family, the sodium chloride and cesium chloride structures. Elaboration has been done on the various models developed and adopted for their study. An introduction has been given to the Harrison's potential, a modified form of which has been used in the present analysis for the study on the alkali-halides.

Chapter four gives the Harrison's formulism in detail and also the modifications effected in the present study. This new form of the potential has been employed to study the properties like binding energy, pressure derivative of bulk modulus, phonon dispersion and elastic constant C_{44}. The mathematical formulism employed have been derived and discussed.

The present study has resulted in the following publications:

(1) Theory of Inter ionic forces in alkali halide crystals, Phys.Stat.Sol.113(b), 339(1982).

(2) Lattice dynamical calculation of the phonon dispersion in sodium halide crystals, Ind.J. Pure.Appl.Phys. 20, 777(1982).

(3) Phonon dispersion in graphite, Presented at the D.A.E.Symposium in Nuclear Physics and Solid State Physics in 1982.

(4) Phonon dispersion relations of graphite and first stage graphite-alkali metal intercalation compounds, Syn.Metals 7, 347(1983).

(5) The phonon dispersion in third stage alkali metal-graphite intercalation compounds, Presented at the D.A.E. Symposium in Nuclear Physics and Solid State Physics in 1983.

(6) Phonon dispersion relations of second and third stage alkali metal-graphite intercalation compounds - accepted for presentation at the International Carbon Conference to be held at Bordeaux, France in 1984.

(7) Phonon spectrum in first stage graphite-lithium intercalation compound - accepted for publication in Carbon (1984).

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