LATTICE DYNAMICS OF THE LAYERED INTERCALATION COMPOUNDS AND QUATERNARY ALLOYS

By

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CERTIFICATE

It is to certify that the thesis entitled "LATTICE DYNAMICS OF LAYERED INTERCALATION COMPOUNDS AND QUATERNARY ALLOYS" being submitted by Mrs. JAISHREE MALHOTRA for the award of the Degree of DOCTOR OF PHILOSPHY in Physics is a record of bonafide research work carried out by her under my guidance and supervision.

To the best of my knowledge the thesis has reached the required standard. The material presented in the thesis has not been submitted in part or full to any other Institution or University for the award of a degree or diploma.

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ABSTRACT

The physical properties of materials having isotropic interatomic interactions along various axes are mostly well understood and these materials are exploited for various technological purposes. Solid state physicists are turning more and more to complex synthetic materials in their search for novel phenomena and potentially useful properties. Many of these materials are highly anisotropic, which is seen as an important property of the layered structures. The studies of the physical propeties of such materials are very few whereas these systems are of great importance from the view point of fundamental physics as well as technological applications of practical considerations.

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 numerous other physical properties. All these properties depend on the motion of the atoms of the crystal and hence their study requires the actual form of phonon frequency spectrum which can be achieved by means of theoretical models of lattice dynamics.

The present thesis has been devoted to the lattice dynamical study of newly developing group of compounds i.e. graphite and its intercalation compounds (GICs) which comprise the first section. In the second section a study of phonons of

chalcogenides and its intercalates has been made. Limited efforts have been made to study III-V quaternary alloys in the third section.

Although the subject of these layered compounds (GICs) is very old [1] and spans the fields of physics, chemistry, material science and others, yet only in the last decade there has been an explosive rebirth of interest due to the availibility of synthetic carbon, commonly referred to as highly oriented pyrolytic graphite (HOPG).

The best example in the class of layered struture is graphite. The key property is its anisotropy which makes it suitable for a wide range of applications. Graphite has a layered structure with the layer stacking sequence ABAB... . The nearest neighbour carbon distance within a plane is 1.42A°, whereas the nearest neighbour interplaner carbon-carbon distance is much larger 3.35A°. It is this disparity in nearest neighbour carbon distance that is responsible for the lamellar properties and weak interplaner bonding. The lattice belongs to the point group D_{6h}^{4} [2] and the unit cell contains four atoms. The forces between adjacent basal planes are nearly two order of magnitude less than those between neighbouring atoms in the same plane[3]. Along the c-axis, bonding is of the van der Waals type and very weak[4].

Graphite can form lamellar compounds with many chemical substances of both atomic and molecular form which may be inserted between the hexagonal carbon planes. These compounds

are classified by the electrical character and structural arrangements of the intercalated substances. There is a wealth of evidence that intercalated atoms or molecules enter the graphite struture as whole layers separated by one or more hexagonal graphite layers [5,6].

Intercalated compounds of graphite are of practical interest because the properties of graphite are drastically altered with intercalation[7]. In addition to their quasi- two dimensional behaviour, fundamental interest centers on their variable anisotropy, which results from the fact that the strength of the interlayer interactions depend upon the nature of the intercalate species.

The earlier studies were mostly done using Born-von Karman force constant model [3,8-11]. Some of these theoretical studies yielded mutually exclusive results, but claimed to prove excellant fits to the available data. This situation resulted due to the availability of only low frequency neutron diffraction measurements of the phonon dispersion curves [3]. But two recently discovered key features provided sufficient information to distinguish valid theory. First, the highest single phonon energy was not at the Brillouin zone center Γ but on the Σ line near the midpoint between Γ and M [12]. Second, infrared reflectivity measurements [13] fixed the zone center A_{2u} out of plane optic mode energy at 868 cm^{-1}.

Maeda et al. [14] and Al-Jishi and Dresselhaus [15] gave

theories to properly account for these new experimental facts. In these models , A_{2u} mode itself was taken as an input parameter in calculation of the force constants, which makes these calculations biased towards the experimental frequencies . Only Gupta et al. [16] first attempted to explain this A_{2u} mode without taking it as an input parameter using de Launy, s angular force model[17]. Their results exhibited a fair agreement with those of the experimental results except a few accoustical branches showing different behaviour. This discrepancy led us to investigate phonon dispersion in graphite.

In the present approach, we have proposed a two body potential for graphite. Interatomic potential approach is found to be better than other approaches as the number of atoms per unit cell is large in the case of graphite. Further, the information available is also limited and it is a few parameter model rather than a few force constant model. In graphite, along c-axis only alternate layers are identical as far as position of carbon atom in a hexagon is concerned, but the present approach assumes all the layers identical which is observed to occur upon intercalation [18]. Thereby the in-plane force constants of graphite could be extended to the intercalation compounds .

The proposed two body potential was given by:

$$\phi(r) = A(r-r_a)^2(r-r_c)^2 e^{-r/\mu}$$

r_a and r_c are the stability distances along a and c axis, A and μ are the Born-Mayer constants. The potential parameters are

fitted with the experimental values of the elastic constants. The dynamical matrix was calculated using first and second in-plane interactions and third out-of-plane interaction using de Launy angular force model. Both central and angular forces were taken into account. Inclusion of the second neighbour angular force constant led to excellant agreement in all directions, especially in the acoustical branches. We have extended our model to calculate phonon dispersion in following graphite-intercalation compounds also:

1.First stage

LiC_6, C_8K, C_8Rb, C_8Cs

2.Second stage

LiC_{12}, $C_{24}K$, $C_{24}Rb$, $C_{24}Cs$

3.Third stage

LiC_{18}, $C_{36}K$, $C_{36}Rb$, $C_{36}Cs$

For these compounds to account for interlayer intercalant interactions, two force constants β_1 and β_1' are incorporated on the lines of Horie et al. [19].

The phonon dispersion, frequency spectrum and elastic constants have been calculated for graphite and its intercalation compounds. A fairly good agreement is found with the available experimental results.

The second part of the proposed thesis deals with the lattice dynamical study of transition-metal chalcogenides and its intercalates.

The transition-metal dichalcogenides and their intercalate complexes belong to a class of the so-called two-dimensional solids in which there is a good deal of interest at present. These compounds are formed in layered structure. Generally, atoms within a layer are bound by strong covalent forces while individual layers are held together by relatively weak forces referred to as "van der Waals " type of interactions. Of particular interest is the possibility of introducing intercalate atoms between the layers which is a unique feature of these low dimensional structures and can be used to change strength of interaction between the layers. It is thus possible to achieve semiconductor to metal and metal to semiconductor transition with intercalation. Layered structure makes these compounds suitable for many practical applications. These compounds can be used for lubrication and hetrogeneous catalysis. These materials are also used in electrochemical photocells [20]. But maximum efforts are concentrated on their use as novel battery system [21-23]. Also the discovery of charge density wave (CDW) instability [24-26] has enhanced the interest in the study of the properties of transition- metal chalcogenides. Experimentally phonons in pure transition metal chalcogenides have been studied extensively [27-30] but few have studied them theoretically.

Verble and Wieting [31] were the first to publish the lattice vibrations of 2H-MoS_2 at Γ point. Bromley [32] explained them using Born-von-Karman model, but met with limited

success as actual structure contains six atoms per unit cell instead of four atoms as used by him. Wakabayashi et al. [33] studied lattice dynamics of MoS_2 using neutron scattering . Axially symmetric [34] and valence force model [35] were used to explain the experimental results but there were discrepancies outside the experimental uncertainties . Feldman [36] explained the published results of $TaSe_2$ [37-40] and $NbSe_2$ [40-42] using a model similar to Wakabayashi et al. with additional parameters.

As few researchers have worked theoretically on these compounds we have taken up the theoretical study of these compounds, These layered compounds can be represented with general formula TX_2 with different co-ordinations between metal and chalcogen atoms. The most significant structure which we have as well studied is 2H-polytype with two layers in the unit cell and trigonal prismatic coordination between transition and chalcogen atoms thus making the lattice hexagonal. In this case Raman spectrum contains interactions related to both interlayer and intralayer.

In the present work, we have studied lattice dynamics of 2H-polytype MoS_2, $NbSe_2$ and $TaSe_2$ using deLauny's angular force model. The central and angular forces are taken into account using α_1 for the first neighbour and α_2, α_2' for the second neighbour within the layer and α_3, α_3' perpendicular to the layer. In order that the crystal remains stable at the nearest neighbour distance α_1 has been taken to be zero. We have solved the dynamical matrix at the Γ point. Out of the ten

frequencies, we have used five frequencies to evaluate the five force constants. Using these force constants, the dynamical matrix is solved in all symmetry directions. In order to test the validity of our model, we have extended our analysis to iron-intercalated niobium selenide also, as done in graphite intercalation compounds.

Lastly, in the third part of the thesis, we have studied viberation spectra of semiconducting quaternary alloys $CdTe_{1-x-y}Se_xS_y$ and $ZnTe_{1-x-y}Se_xS_y$. Current interest in studying the properties of mixed crystals is due to their wide applications in a variety of optoelectronic devices. Their energy gap can be arranged over the important wavelength range that conveniently spans the region of minimum loss in optical fibres and at the same time a lattice match to the substrate can be maintained by keeping $y/x = 0.22$. Importance of these compounds led us to obtain information concerning the solid state properties of concrete solid solutions of this type and to elucidate how the theoretical model applicable to binary and ternary mixed systems may be used for the quaternary mixed system.

We considered a zinc-blende lattice formed by two interpenetrating sublattices numbered 1 and 2 occupied by four types of atoms A, B, C and D in a way that corresponds to the situation in the mixed system $AB_{1-x-y}C_xD_y$. Sublattice 1 is occupied by atoms of type A and sublattice 2 is occupied by

atoms of types B, C and D . K_1 , K_2 and K_3 are the nonrandomness parameters for the mixed system $AB_{1-x}C_x$, $AB_{1-y}D_y$ and AC_xD_y $(x+y=1)$ respectively and are introduced in such a way that in a mixed $AB_{1-x}C_x$ system, (1-x)B atom will interact with (1-x)B atom as well as K_1 xC atoms; similarly xC atom will interact with xC atom as well as with K_1 (1-x)B atom. Along similar lines, the nonrandomness parameters K_2 and K_3 are taken into account for the mixed $AB_{1-y}D_y$ and AC_xD_y $(x+y=1)$ crystal system. The dynamical matrix for the multi component system $AB_{1-x-y}C_xD_y$ can be written along the similar lines as in ternary $AB_{1-x}C_x$ mixed system [43-44]. If x and y are zero, the dynamical matrix reduces to a 2x2 matrix giving the phonon frequencies of the binary(AB) system only. For the sum of x and y $(x+y=1)$ equal to unity the matrix equation reduces to 3x3 matrix giving phonon frequencies of the ternary AC_xD_y system and for other values of x and y, the dynamical equation gives phonon frequencies of the quaternary $AB_{1-x-y}C_xD_y$ mixed system. A linear variation of x from Vegard's law [45] has been considered for evaluating the constants for the ternary and quaternary mixed systems.

The present study has resulted in the following publications:

1. Lattice dynamical model and its alkali metal intercalation compounds.

   H.C.Gupta, Jaishree Malhotra, Neelima Rani and B.B.Tripathi.

   Phys. Rev. B33, 7285 (1986).

2. Phonons in graphite and LiC_8.

   H.C.Gupta, Jaishree Malhotra, Neelima Rani and B.B. Tripathi.

   Material Science and Engineering 85, 187 (1987).

3. Optical phonon frequencies in the quaternary $CdTe_{1-x-y}Se_xS_y$ mixed system.

   H.C.Gupta, Geeta Sood, Jaishree Malhotra and B.B.Tripathi.

   Phys.Rev. B34, 2903(1986).

4. Phonons in graphite and the alkali intercalation compounds.

   H.C.Gupta, Jaishree Malhotra, Neelima Rani and B.B. Tripathi.

   CARBONNE 1986 (Proc. of the International Carbon conference 30th June -4th July 1986, Baden-Baden, West Germany.)

5. Phonon dispersion in graphite using a two-body potential approach.

   H.C.Gupta, Jaishree Malhotra, Neelima Rani and B.B.Tripathi.

   Solid State Comm. 57, 263 (1986).

6. Long wavelength optical phonons in $ZnTe_{1-x-y}Se_xS_y$ quaternary alloys.

   H.C.Gupta,Geeta Sood, Jaishree Malhotra and B.B.Tripathi.

   Seventh Conference of the CMD-EPS, Italy (1987).

CONTENTS