A LATTICE DYNAMICAL STUDY OF METALS AND SEMICONDUCTORS

by

M.V.N. AMBIKA PRASAD

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Department of Physics
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
110016

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DEDICATED TO MY PARENTS

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M.V.N. Ambika Prasad

(M.V.N. AMBIKA PRASAD)

PREFACE

Lattice dynamical studies of solids are a pre-requisite for a proper understanding of numerous properties of solids. The present work has been devoted mainly to the theoretical study of hcp transition metals, alkaline rare earths and lanthanides in the first part and semiconductors having zinc-blende structure in the second part. Microscopic approach has been adopted for the case of metals whereas for semiconductors, we have used a phenomenological model. The first part of the thesis deals with the pseudopotential approach. During the past two decades or so, the lattice dynamics of metals has received considerable theoretical and experimental attention, especially because of the presence of conduction electrons. Many theories have been developed to interprot the experimental data. Particularly, the case of metals has been very interesting, because of the role of electron-ion interaction. Phenomenological theories developed to incorporate electron-ion-interaction have met with limited success. These models have not explained satisfactorily the observed anomalous behaviour of transition metals.

The concept of pseudopotential, 'a weak and effective electron-ion interaction potential' has emerged as a very successful tool representing the electron-ion interaction. The pseudopotential approach has been applied quite successfully in interpreting atomic, electronic and numerous other electrical and thermal properties of metals and has been instrumental to interpret the phonon anomalies of transition metals[1-4].

Encouraged by the success of the pseudopotential approach in simple and noble metals, it is thought worthwhile to test the formulation to transition metals. In our present study, lattice dynamical properties for the following metals have been investigated.

(i) hcp transition metals - Titanium, Zirconium and Hafnium

(ii) Alkaline rare earths - Calcium, Strontium and Barium

(iii) Lanthanides - Lanthanum, γ-Cerium and Yttrebium.

In the case of hcp transition metals, Titanium, Zirconium and Hafnium, investigations have been carried out to study their lattice dynamical properties by using the transition metal model potential as given by Nand et al.[5]. The d-state radius dependent effective mass[6] has been incorporated in the electron phonon interaction matrix element within the pseudopotential framework. In the evaluation of phonon dispersion curves, there are two contributions to the dynamical matrix elements, namely, electrostatic contribution and electronic contribution. The electrostatic part of the dynamical matrix elements arises from the Coulumbic interaction between the ions, immersed in a uniform compensating negative charge and can be evaluated on the lines of Kellermann[7]. The electronic part of the dynamical matrix element is calculated using the local field correction due to Hubbard[8] (Falicov and Heine). In general, the results obtained here are in good agreement with experiment[9-11]. More important is the reproduction of the anomalous behaviour of the softening of the [0001]LO branches in all the hcp transition metals,

namely Titanium, Zirconium and Hafnium, as observed experimentally. Also, when compared with Animalu's results, results obtained here are much better. Animalu's potential does not reproduce the softening of the [0001] LO branch in any of the hcp transition metals investigated here. In general, the present approach within the pseudopotential framework is satisfactory enough to justify this effort as a microscopic calculation of phonon dispersion curves in Titanium, Zirconium and Hafnium. We have also used this transition metal model potential to study other solid state properties like binding energy in the solid state and electrical resistivity and thermo-electric power in the liquid state.

The lattice dynamics of alkaline rare earths, namely Calcium, Strontium and Barium have also been investigated here by applying the model potential of Nand et al. to them, to interpret their phonon dispersion by using the local field corrections given by Hubbard[8] and Singwi et al.[13]. The phonon frequencies obtained here are in good agreement with the experiment[14], thereby establishing the validity of the model pseudopotential framework for these metals. The anomalous dispersion is exhibited better by the present model pseudopotential including local field correction due to Hubbard (Falicov and Heine)[8]. Investigations have been carried out here to study other solid state properties like binding energy and thermo-electric power and electrical resistivity in the liquid state.

The lattice dynamics of Lanthanides namely, Lantharum, γ-Cerium and Yttrebium have also been investigated here. The

phonon dispersion curves and other properties of these metals have been calculated in the same lines as was followed for the alkaline rare earths, using both the local field corrections namely, those of Hubbard[8] and Singwi et al.[13]. The phonon frequencies obtained here are in good agreement with the experiment[15-18]. In the case of γ-Cerium, no anisotropy has been observed with both the local field corrections. However, in the case of Lanthanum the anomalous dispersion and anisotropy is better exhibited by the Singwi et al. local field correction. In the case of Yttrebium, anisotropy with regard to the propagation of elastic waves has been observed. Therefore, it has been concluded that the pseudopotential treatment has been successful in explaining the lattice dynamical properties of hcp transition metals, alkaline rare earths and lanthanides.

The second part of the thesis deals with the elastic force model approach and is based on the Born-von-Karman theory of lattice dynamics. Recent developments in the field of semiconductors have generated widespread interest to study them experimentally and theoretically. Earlier strong emphasis were laid on elemental semiconductors. But, of late, particularly from the last two decades or so, extensive studies have been made experimentally and theoretically on compound semiconductors like zinc chalcogenides and III-V semiconductors[19-22]. Most of the results of the physical properties of these compounds have been explained by some phenomenological model or other. The present investigations are on the lattice dynamics of III-V and II-VI semiconductors having the zinc-blende structure, within the

modified rigid ion model framework, accounting the effect of polarizability explicitly, involving four force constants α_1, α_2 for first neighbour and α_1' and α_2' for the second neighbour, respectively. It is observed that the effect of polarizability leads to a marked improvement, especially in the lattice dynamical study of zinc-blende crystals, where the value of dielectric constant is large. In the present studies, the dynamical matrix consists of, in addition to the electrostatic contribution[7], with the inclusion of effective charge, the repulsive contribution up to second neighbours. The effect of polarizability has been accounted explicitly, assuming both ions to be polarizable[23]. The model parameters are determined by the knowledge of elastic constants and experimental phonon frequencies. Using these model parameters the phonon frequencies are determined by solving the secular determinant.

II-VI Semiconductors

These semiconductors are partially ionic, crystallizing in zinc-blende structure, having small energy gap and high dielectric constant. To account for the ionic character of these compounds, an effective charge (z_{eff}) is assigned to these ions, on the basis of Lydanne-Teller (LST) relation[24]. The lattice dynamical properties of zinc-chalcogenides namely, ZnS, ZnSe and ZnTe are investigated using the above model. A calculation is carried out to obtain phonon spectrum and the specific heats. The results obtained here are in good agreement with the experiment.

III-V Semiconductors

The calculations are carried out to obtain the phonon spectrum and specific heats for this type of semiconductors, namely GaP, InSb and InAs, in the same lines as was followed for II-VI semiconductors. It has been found that the results obtained here are in good agreement with the experiment.

The investigations have resulted in the following publications:

1. Effect of polarizability in the phonon spectrum of zinc-blende compounds - Physica Status Solidi (b), 114, K 11 (1982).
2. Lattice dynamics of γ -Cerium using a model potential approach - Nuclear Physics and Solid State Symposium, Solid State Physics, 26 C (1983).
3. Lattice dynamics of Calcium and Yttrebium using a model potential approach - Phy. Rev. B 29 (1984).
4. Phonon anomalies in hcp Hafinium (communicated).
5. Phonon anomalies in hcp transition metals using a model potential approach Can. J. Phys. (1984).
6. Lattice dynamics of γ -Cerium and Lanthanum using a model potential approach (communicated).

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