LATTICE DYNAMICS OF SEMICONDUCTORS AND METALS

by

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PREFACE

Semiconductors have been instrumental in the development of solid state techniques, both theoretical and experimental. Phenomenological theories have been developed which provide valuable models for the interpretation of experimental results (such as electronic energy bands, electron-phonon interaction, lattice vibrations etc.).

Various models have been proposed in recent past to study these materials, but detailed theoretical investigations were lacking due to the limited experimental data. The models generally employed were the rigid-ion model, the shell model, the force-constant model etc. Shell model tends to have a greater number of parameters for which large number of experimental data is needed. Cochran et al. (1966) recently, in the study of the lattice dynamics of lead telluride, remarked that the shell model usually gives very good results in the case of alkali halides and is far less satisfactory for lead telluride than for sodium iodide or potassium bromide, since many more parameters are required to obtain adequate agreement with the experimental results. This model normally fails for materials with high dielectric constant and small energy gap between the valence and the conduction band.

Rigid-ion model in its simplest form as employed by Kellerman (1940) is inadequate as it leads to $C_{12}=C_{44}$. Recently the concept of angular forces have been well adopted to account for Cauchy discrepancy, following the pioneer work of Varshni and his co-workers (Yuen and Varshni 1967). They considered the presence of angular forces along with central forces to explain the lattice dynamics of fcc metals (copper). They adopted both the approaches, one due to Clark, Gazis and Wallis (1964) (CGW) and the other due to de Launay (1956) (DAF). They obtained satisfactory results. Behari and Tripathi (1970) and Bose et al. (1973) extended their studies to include several fcc, bcc (including transition metals) and hcp metals and the model was uniformly successful. More recently Varshni et al. (Banerjee and Varshni 1969) have proposed a rigid-ion model to explain the lattice dynamics of III-V compounds.

The proposed thesis includes investigations on lattice dynamical properties of some of the semiconductors and some metals. In the present work we have formulated a rigid-ion model where angular forces are also incorporated to account for the Cauchy discrepancy. The superiority of this model over others is that while containing a fewer number of parameters it is able to interpret the lattice dynamics of a large number of compound semiconductors.

Angular Forces: These have been included through two approaches (i) due to de Launay (1956) (DAF) and (ii) due to Clark, Gazis and Wallis (1964) (CGW). In DAF type the restoring force arises due to the angular deviation of the line joining two atoms from its equilibrium position. The force is perpendicular to this line and lies in the plane of the deviated and the equilibrium position of the line. In CGW type the restoring forces are called into play due to the deformation of all the three angles of a triangle formed by an atom with its neighbours.

Modified Angular Force Model: The angular force models of the DAF type and the CGW type have been developed for sodium chloride and zinc sulphide structure. In the present work IV-VI and III-V compounds have been studied in detail. The total interatomic forces are supposed to consist of four parts: (i) the central forces between the ions which act along the line joining the two ions, this has been taken on the lines of de Launay, (ii) the angular forces between the ions (on the lines of de Launay and Clark et al.); (iii) long range Coulomb interaction between the ions, treated in the spirit of Kellermann and (iv) the overlap repulsion between the ions, short range in character, also on the lines of Kellermann.

The secular determinant of the modified angular force model has been set up. The model parameters are determined by the knowledge of zone centre frequency, elastic constants and zone boundary frequencies.

IV-VI Semiconductors: These semiconductors are partially ionic, crystalize in sodium chloride structure and are characterised by small energy gap, high dielectric constant and large electronic polarizability. To account for the ionic character of these compounds an effective charge Ze is assigned on the ions. On the basis of the above model, the lattice dynamical properties of PbTe, PbSe, PbS and SnTe are evaluated. The total number of parameters are seven which have been reduced to six by choosing an appropriate ratio between the two repulsive force constants, the remaining being calculated with the knowledge of the elastic constants and the zone centre frequencies. A calculation is carried out to obtain phonon dispersion relation, phonon spectra, and the (θ - T) relation. The results obtained using the two alternate approaches of angular forces to yield somewhat different results on phonon dispersion curves but not for other dynamical properties. The agreements with the experimental results (wherever available) are fairly good.

III-V Semiconductors: These types of semiconductors

crystalize in zinc blende structure. These compounds also have small energy gap and large high-frequency dielectric constant and have partial ionic character. An effective charge Ze is assigned on ions to account for the ionic character of the compounds. On the basis of the above mentioned model, the dynamical properties of GaAs, GaSb, InAs, InSb, GaP, AlSb are evaluated. The total number of parameters being seven these are obtained by the knowledge of zone-centre and zone-boundary frequencies or zone-centre frequencies and elastic constants. The results are obtained for dispersion relation, phonon spectra and (θ - T) relation and it has been found that they agree fairly with the experimental results (wherever available). All the calculations have been done using both the approaches of angular forces.

A few metals and elemental semiconductors have also been studied using angular force models and pseudopotential method.

Metals: Angular force model is applied in the study of dynamical properties of some fcc and bcc metals. The conduction electrons play an important role in the binding of metals, these electrons give rise to volume forces. The model developed by Behari et al. (1970) has been applied to study the lattice dynamics of Rb, Cs and Pt. Phonon dispersion relations, phonon spectra, (θ - T) results and Debye-Waller factor calculations offer a

good agreement with the experimental data. A study of the solidified xenon has also been carried out on an angular force model. The results agree well with the experiment.

Pseudopotentials: Recently pseudopotential concept has been widely applied to the study of metals and has met with reasonable success. A three parameter model potential

$$W_b(q) = \frac{1}{\Omega_0}\left(-\frac{4\pi Ze^2}{q^2} + \frac{\beta \sin qr_c}{(1+(q\gamma_c)^2)^2}\right)$$

is proposed for elemental semiconductors (Si and Ge). The parameters have been determined by fitting the effective potential for three experimental values of Fourier coefficients obtained from Fermi surface data. For screening of bare-ion potential a modified form of the Hartee dielectric function due to Srinivasan (1969) has been used. A calculation of the form factor, binding energy liquid state properties and band gap has been made. The results are in good agreement with the experiments.

On the basis of the above model, calculations have been made in the case of metals. The parameters of the model potential have been reduced to two by putting $\gamma_c = r_c$ and the remaining parameters are obtained by experimental Fermi surface data. The results are obtained for form factor, binding energy, liquid-state properties in the

case of Pb, Al, K and Na. The agreement between theory and experiment is good.

The investigations have resulted in the following publications:-

1. Effect of angular forces on the crystal dynamics of solidified xenon, IL Nuovo Cimento 10B, 1972, 111.

2. Crystal dynamics of some cubic metals on an angular force model, J.Phys.F: Metal Phys. 4, 1974, 11.

3. Some electrical properties of silicon and germanium on a pseudopotential approach, J.Phys.C. (Solid St. Phys.) 7, 1974, L134.

4. Crystal dynamics of IV-VI compounds (communicated).

5. Modified angular force model for the crystal dynamics of III-V compounds (communicated).

6. Study of Al, Pb, Na, K- a Pseudopotential approach (communicated).

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