Brief Review of Lattice Dynamical Models for Zinc-Blende Crystal

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Various theoretical models for the lattice dynamics of tetrahedral bonded crystal having zinc blende structure have been proposed by different workers.The crystals which are tetrahedral bonded are formed mainly from the Elements of II,III,IV and V group of periodic table . These crystals, which have two interpenetrating , face centered crystal lattice are II-Iv, III-V, IV-IV compounds. These crystals are partially co-valiant and ionic' in bonding except diamond. The lattice dynamical models proposed to describe different interactions inside the crystals should be physically consistent with the nature of bonding in them. The present chapter gives a brief account of different interatomic force models proposed earlier by different workers to describe the lattice dynamics of Zinc blende crystals. Some important force models are described in subsequent sections.

Rigid ion model (RIM):

The foundation of the lattice dynamics of solid was laid by Born under a rigid ion approximation . In the rigid-ion-model, ions are regarded as the rigid and unpolarizable point ions and they are prevented from collapsing under mutual coulombs attractions by the presence of a short-range overlap repulsion. Hence this model is often called the rigid ion (or point ion) model.

When the lattice is distorted during vibration the ions get displaced and may be represented by dipoles placed at the perfect lattice sites. This cause a change in the lattice energy due to dipole-dipole interaction summed over all the range in character it is difficult to truncate by Kellerman[2] using the technique proposed by Ewald[3] from the calculation of Madalung energy. According to RIM approximation the potential energy of interaction of ions separated by a distance.

The rigid ion model fails in explaining the dielectric behaviour of the ionic crystals. As this model considers the ion to be rigid and unpolarizable , the high frequency   dielectric constant $\varepsilon\infty$ must be equal to unity for all ionic crystals. Experimentally it is found to be incorrect.

Another defect o rigid ion model is that the value of the longitudinal optical frequency L_o obtained by this theory and by LST(Lyddane-Sachs-Teller)[4] relatively.

It is seen that experimentally quantities fails to satisfy the relation. Szigeti[5-6]suggested the replacement of k by the effective compressibility and by the effective charge es*(=Ze) respectively. The ratio es*/e is found to be less than unity.While X Ray diffraction studies show that ionic charges of the alkali halides (except LiF and NaF) are not much different from effective ionic charges. So Szigeti suggested that apart from the ionic and electronic polarization, there is some further polarization of opposite sign which has not been included the attributed this polarization to the mutual distortions of neighbouring ions owing to their overlap. The effect can be described in terms of the multiple moments which appear on the ions due to the redistribution of the charge in the overlap region. These dipoles are termed as the "distortion dipoles".

Modified Rigid Ion Model (MRIM):

This model was first proposed by Vetelino Mitra'[7] and later on developed by their Co-workers [8-9]. It is essentially a Rigid ion model which incorporates (a) the short range central and non-central interactions and (b) the long range Coulomb interaction among ions of appropriate effective ionic charge, which ensures a proper L_0-T_0 mode splitting. The development of this model is thus based on the concept of Szigeti [5-6] effective charge. The expression for the crystal energy and secular equation corresponding to MRIM are almost the same as those given, rigid ion model except the difference in the definition of ionic charge (ze) and the extension of short range focus upto second neighbor ions. Also the values calculated for the effective ionic charge are not much different from the Szigeti effective charge for most of the crystals

Clark, Ghazis and Walls Rigid Ion Model:-

The harmonic force which arise due to the displacements of the atoms can be classified into several categories one of the most important of these is the central force that acts only among the line joining any two atoms and is therefore radical force. The mechanical analogy is a spring whose restoring force is proportional to the charge in length of the spring and is independent of the angular deviation of the spring from the line connecting two atoms.

Another type of force depends on the angle which the line joining the moving atoms makes with the equilibrium position of the line. This is referred to as an angular force. The mechanical analogy is a rod connecting the particles the rod being fastened at it's end equilibrium position by rod being fastened as its end the equilibrium position by spring perpendicular to the rod. The combination of central and angular force is known as non-central force.

The angular forces have been used in literature in two distinct ways both of which owe their inspiration to Born's early work. One of these has been discussed at length in De Laundry's [10] review article. Such angular force are sometimes referred to as De Laundry's type of Angular force. The other method was originally used by Born and Later by Nagendra Nath[11] and other workers of the Roman School. It has been recently discussed and used by Clark, Ghazis and Walls[12]. The angular forces used in this method are very often called C.G.W. type of Angular force.

If the angular forces are included in this way the same value of compressibility is obtained whichever of the two methods mentioned earlier is used for computation. Obviously the C.G.W. method of using the angular forces is more satisfactory than of De Laundry.

Rigid Shell Model:-

   In recent years there has been considerable success in the application of the Rigid Shell Model (RSM) picture to describe the lattice libration of ionic or covalent crystals. Dick and Overhauser[13] originally developed the model to calculate the effective ionic charge Es *, which is the measure of the strength of the electric dipole absorption of the infrared radiation by crystal lattice vibration.

In the shell model each ions has a rigid core formed by the molecules and the inner tightly bound electrons. The core is surrounded by a 'rigid' shell of electrons. Each shell being bound to its core by an ideal spring. Adjacent shell also interact with each other via springs. As a result of the shell-shell inter-action , the ions deform during a vibration i.e. there is a displacement of the electrons shell relative to the ion core. This leads to an additional dipole moment at each ion site whose magnitude is determined by the electric polarizability of the ion. Since the polarizability of the negative ion is usually greater than that of the positive ion the net contribution of the additional moments is opposite to the moment arising from the displacements of the cores. One also takes into account the exchange charge in the region of overlap of the electron orbitals. The change charge which is positive, arise from the redistribtution of electrons in the region of overlap .Such redistribution occurs because of Pauli exclusion principle. During a lattice vibration the exchange charge also makes a contribution to the dipole moment. Later, it was Cochran who developed shell model into a theoretical scheme to study the lattice dynamics of crystals. He used the model to study the dispersion curves of germanium and found that the theoretical dispersion curves were in fair agreement with the experimental dispersion curves. Cochran [14-15] and Woods[16] used a simplified version of the shell model to study the dispersion curves of NaCl. An experimental investigation of the dispersion relations for sodium iodide has given results in good agreement with calculations based on shell model, despite the fact that the theory contains no parameter which may be adjusted to fit the data obtained by neutron spectroscopy.

                  The use of the shell model gives the atom the property of polarizability in an electric field and of distortion polarizability under the influence of short range forces acting through both cores and shells. The lattice vibrations, therefore, include electric field in the crystal. The existence of dipole moments is attested by the infrated absorption of germanium and these moments results in a long range interaction between ions. The fact that the shells are taken to be coupled to nearest-neighbour shells, and to have negligible mass introduces a further long range force of non-electrostatic character. The electrostatic interaction in germanium has been taken by Lax[17] to be quadrupole interaction because , although dipole moment may exist on the atoms during vibration. The total dipole moment of the crystal must vanish because of the space group symmetry of germanium.

Exchange Charge Shell Model

The short-range polarization mechanism implied in RSM has revealed that this mechanism alone is not adequate to describe the dielectric behaviour of ionic crystals. This limitation led Dick and Overhauser[13] to postulate and additional polarization called the exchange charge polarization. This polarization mechanism owes you it's origin to Pauli exclu exclusion principle which acts to reduce the electron charge destiny of the ions in the overlap region and hence leads to redistribution of of the charge on the ions. This gives rise to a charge depletion which may be represented as the superposition of point charge of suitable magnitude called the exchange charge considered to be located at the center of gravity of overlap region. The dipole moment permit volume associated with this mechanism is called as the exchange charge polarization.

Variable Charge Shell Model (VCM):-

The fundamental concept of this model was developed by Feld Kamp[27] for zinc-blende structure. According to this model the shell-shell charge, during vibrations varies with the nn distance as

where each ion is regarded to consist of a core μ' of charge $Z(\mu')$ c and a shell μ' of charge $Y(\mu'')$ e where lel as the electronic charge. Here (μ_{11}^m) represented the μ'' shell in Cell. $\mu f(r)$ is a function of distance (r) and tend to become zero as r→∞. R ($\mu_{11}^m v_{11}^m$+p) is a vector distance of the nn shell from the shell (v_{11}^m+p) from the shell (v_{11}^m). The overlap repulsion is is taken to be central and to act only through the shells. This inclusion of charge-transfer from one shell to another has given rise three and four body forces.

Bond Charge Model:-

The bond charge model developed by Martin [41,42] is an outcome of the generalization of the Bond-charge concept of Philip[43] .The electronic polarization in it assumed to arise from the bond charge (BC) which are situated at the center of the covalent bonds and assumed to stay half way between the atom during their movement. The BC's interact with the ion cores and with each other via is pure Coulomb potential.

The self interaction of a bond charge with itself has been excluded and this assumption is equivalent to the inclusion of the exchange and correlation effects. Martin has regarded each BC to split into two, each half moving with one of the atoms associated with the bond. The contribution to dynamical matrix due to the motion of these BC's against the rest of the lattice comes out to be dependent of $\vec{q}$, since they are not situated at the lattice sites.

The Martin's BCM is apparently very much similar to the Hardy's DDM and suffers from several limitations which has been pointed out by Sinha[44].

Weber[45] has extended this approach to tetrahedrally co- ordinated semi-conductors and has derived the dynamical matrix of his BCM treating the BC's as independent lattice particles.

This model involves four parameters corresponding to the four types of interaction (1) a central potential between nearest neighbour ions (2) Coulomb point charge at the sites of the ions and the bonds,(3) central potential between next neighbour ions and BC's and (4) the interaction between two adjacent bonds described by Keating potential.[46]

The key feature of this model is that the very flat TA branches in covalent crystals are understood in terms of the weak effective ion. BC forces Weber and Rustogi[47] extended the adibatic BCM to described phenon dispersion relations and elastic properties of III-IV. Semi-conductors.A symmetry of the bond charge charge position and the force constants involving them is found to be them main consequences of ionicity.

Pseudo Potential Approach:-

Soma & Co-worker[5o-53] formulated theory for the lattice Dynamics of group . Semi conductors according to the Jones-zone scheme proposed by Heine and Jone and also obtained the bulk properties of the tetrahedrally bounded compaund in good agreement with observed data. Recently. Soma and Kagaya[54] extended the treatment by including partially ionic interactions.

The model pseudo Potential of Ashcroff and the local modal potential of Heion Abarenkov were used by Soma and Kagaya in calculating phonon dispersion relations of several zinc blende compaunds. The dielectric constant of Hubbard was considered.

Velence Bond Binding Model (VBBM):-

Vasilev et .al[57] introduced bond blending force model for the lattice Dynamics of diamond structure crystals. This model to be known as valence Bond Bending Model (VBBM) has been used for describing the "covalent nature of bonding in zinc-blende structure by Ram and Kushwaha [5]. The sp^3 valence electron wave functions are known to be hybrided into four direction orbitals overlapping of such two orbitals leads to be covalent binding in solids.

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