



# BINDING FORCES IN TETRAHEDRALLY BONDED SEMICONDUCTORS

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*It can be observed from the preodic table that the group IIIb atoms have three electrons. With an  $s^2p^1$  configuration outside a core of closed shells, and that group Vb atoms have five electrons in  $s^2p^3$  configuration. Between them, therefore, the III and V atoms have an average four valence electrons per atom available for binding. III – V compounds with the zinc blende structure do indeed have properties rather like those of the group IV crystals, diamond, silicon, germanium and grey tins in which covalent bonds are formed between tetrahedral  $sp^3$  hybrid orbitals.*

*Though in III – V compound there the correct electrons per atom to form tetrahedral covalent, the two kinds of atoms will not in general have the same electronegativity or the same size, and so we might except a some what different bonding scheme from that of the group IV element. Let us consider three idealized possibilities covalent binding. 'ionic' binding and neutral binding.*

*For covalent binding, each V atom donates an electron to a III atom. So that  $V^+$  and  $III^{-1}$  ions are formed, each with four valence electrons. These combine into  $sp^3$  hybridization and tetrahedral bonds are formed as in diamond. There will, however, be an additional electrostatic attraction between the charged ions. For*

pure ionic binding we may suppose that the III atom donate three electrons to the V atom forming  $III^{3+}$  and  $V^{3-}$  ions, each with spherical symmetrical closed shell configuration. These ions would be held together in the crystal by purely electrostatic forces. In the neutral bond proposed by Slater and Koster<sup>34</sup>, the third atom retains three electrons and V atoms five so that there is no charge difference between the atoms. These three bonding schemes represent simply ideal cases and actual bonding will not correspond exactly to any one of them. It appears that the bonding in III – V Zinc blende structure crystals is near to the neutral bonding schemes but with a varying degree of charge difference between the III and V atoms in the different compounds.

We may write the approximation to the wave function of the valence electrons in a III-V crystal by means of combination of idealized states. We can write for wave function of a III-V bond as

As ion increases relative to a covalent bond becomes polarized towards the V-atom, and the certain value of  $a_{ion}/a_{cov}$  will result in a charge difference between the III and V atoms (sometimes loosely referred to as the ionicity of the bond). By the vaporization principle (PI) the best value of  $a_{ion}/a_{cov}$  is giving the minimum value of the energy corresponding to III-V. theoretical calculation by Coulson, Radej, and Stoker for cubic boron nitride give the result that the covalent BN bonds give a net excess charge on each N – atom of about one third of an electrons. This correspond fairly closely to the neutral bonding scheme of Slater and Koster but with a slight excess of electrons on the V atoms. We should at this point consider what we mean when we speak of the charge on an atom in a crystal. Suppose we take the charge to mean the net charge inside a volume which enclose the atom. In an ionic crystal this concept is valid because the electron density falls to a low value between neighbouring nuclei, so that there is no clear boundary at

which one atom ends and the next begins. Consequently there is not obvious volume surrounding each nucleus within which to consider the net charge, and the charge well depend on the size of the volume closed. A large volume will enclose more electrons and increase the negative part of the charge balance. In III-V compounds, we would consider the net charge inside a sphere having the covalent radius of the atom or we might prefer to imagine the crystal divided into equal polyhedral cells centered at each atom. We conclude therefore that we cannot attach the absolute value to the charge on the atoms in these crystals, which have a degree of covalent binding, because we do not know the relative volumes of the III and V atoms. On similar arguments in II-VI compounds covalent bonds are formed between tetrahedral  $sp^3$  hybrid orbitals.

It is well known that the compounds of the alkali metals with the halogen elements are crystalline solids, which are of great interest, from both the theoretical and experimental standpoints. Sixteen of them, viz., the compounds of lithium, sodium, potassium and rubidium respectively with fluorine, chlorine, bromine and iodine possess crystal structures similar to each other, the typical case being rock-salt or NaCl. Alkali halides are relatively easy to subject to theoretical treatment since they have simple structure and are bound by the well understood coulomb forces between the ions. The alkali halides have special significance in chemistry since they are the simplest known 'ionic' molecules. Many physico-chemical parameters of these crystals are directly connected to the binding forces in ionic solids. One of the fundamentals problem in the theory of solids is the calculation of the binding energy of the crystal it plays an important role in understanding nature of inter-ionic forces and of their effects thermal, elastic and anharmonic properties. The lattice energy of ionic crystals is an important parameters, directly connected to the binding forces in ionic solids. The

*theoretical treatment of ionic lattice energy was first made by Born and Lande. There have been several theoretical models dealing with the estimation of lattice energies in ionic crystals, apart from the experimental method based on the Born-Haber cycle. Comprehensive reviews of lattice energy calculation have been given by Waddington.*

*From these models show remarkable deviation from the experimental values in most cases. In view of this an effort was made in our earlier communication 10 to report and study a new and relatively simple correlation for ionic crystals, from the electronegativities of the constituent atoms of the crystal. It was well established that effective ionic charge concept is strongly related to the elastic binding can be understood from the concept of electronegativity. Moreover bond energy and electronegativity is well correlated. A cyclic process has been devised by Born and Harber<sup>1-9</sup> while relates the crystal energy to other thermochemical quantities. Bond energy or dissociation energy is one of the parameters involved in Born- Haber cycle. The above Correlation will provide the direct link between lattice energy and bond energy. Reddy et al. 10 have established a good correlation between lattice energy and electronegativity. With this in view a simple relation has been proposed to evaluate lattice energy of crystal utilizing the concept of bond energy. The lattice energies are calculated on the basis of such an approach have been found to show agreement with experimental values.*

*A number of crystalline which can be determined on the basis of theoretical backgrounds provided by the study of Lattice Dynamics of the solids. The influence of the vibration of atoms in crystals on the thermodynamic properties of solids and the relation of microscopic elastic properties of a crystal with atomic force constants, which determine the scale of lattice vibrations at a given temperature have been the subject of considerable study in the recent days.*

*The vibration of atoms in a crystal determines the thermal properties and governs the phenomena like diffuses scattering of X- rays, neutron scattering, spin scattering relaxation and many more other properties. the most direct measure of the localized motions of a given atom in a solid are its position and momentum distributions functions, Debye<sup>7</sup> and almost simultaneously by Max Born and Won Karmen<sup>8</sup> removed the discrepancy between Einstein's theory and experiment for specific heat at low temperature. Debye's theory was remarkably successful in explaining the temperature dependence of specific heat of most metals at low temperatures. But the theory was unable to explain the behavior of specific heat at low temperature for graphite, bismuth, selenium and tellurium. Due to availability of high intensity thermo neutron beams from nuclear reactors, it is possible to study processes involving single lattice wave and the frequency distribution function and the dispersion relation.*

*The thermal diffuse scattering of X- rays by the atomic vibrations of a crystal and the coherent in elastic scattering of thermal neutrons by one phonon processes permit the determination of the frequencies of individual normal modes of a perfect crystal similarity experiments involving the absorption or scattering of light by crystals containing impurity atoms provides the frequencies of various types of exceptional vibrational modes induced by these impurities and defects. The frequencies of exceptional, impurity induced, normal modes of the crystal can also be observed in the phonon side bands to the absorption or emission spectra associated with electronic transitions at impurity centre in crystals. Vibration of crystals lattice give rise to an interacting between defects and boundaries in addition to the interaction that exists due to the overlapped of their elastic strain fields. The theory of localized properties of lattice vibrations is more difficult than that of thermodynamic quantities of the vibration, while the formal seeks the*

*vibrational properties of individual atoms or individual normal modes. A large number of models regarding the nature of inter atomic interaction in solids has been proposed for describing the vibration of atoms in lattice. Different theoretical models of lattice dynamics was found to be of paramount importance as they give and understanding of the vibrational, thermo dynamical, elastics, optical, electrical and other physical properties of imperfect crystals.*

*Fundamentally the dynamical theory of crystals is a many body problem involving a large number of electrons interacting with ions constituting the lattice and cannot be solved explicitly. Thus it is necessary to adopt certain approximation in solving the problem. The approximation adopted in developing the general theory of lattice dynamics are the adiabatic approximation and the harmonic approximation.*

*In adiabatic approximation, electrons in metallic crystal are treated to response so quickly to the motion of ion that there state is always just a function of the ionic coordinates. Thus adiabatic principles allow to separate the ionic motion from electronic motion, leaving only a residual interaction between the electrons and phonon. In this way the electrons and the lattice waves are treated as nearly independent entities and the electrons are allotted the same coordinates as those of ions.*

*In harmonic approximation the forces of restitution, which operate during the vibrations of atoms are assume to be the proportional to the displacement of atoms. The force of restitution called harmonic forces are evident in the following ways :*

1. The atoms are assumed to be connected by imaginary springs, under Hooke's Law of forces. In actual calculation these forces are represented by ad hoc Hooke's constants.
2. The interaction potentials are defined for the interaction in the solids and the forces are derived from these potentials.

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