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A Study of Bonding and other Related Properties of Some Rutile type Oxide Crystals.

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A STUDY OF
BONDING AND OTHER RELATED PROPERTIES
OF
SOME RUTILE TYPE OXIDE CRYSTALS.

A Thesis Submitted

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For

The Degree of Master of Philosophy

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By

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Dated : 20.4.89

DECLARATION

This is to declare that the major portion of the dissertation submitted for the degree of Master of Philosophy to Rajshahi University is based on my investigation and was carried out under the supervision of Professor A.K.M. Azharul Islam, Department of Physics, Rajshahi University.

The work embodied in this thesis has not already been submitted as a thesis in substance for any degree and has not been concurrently submitted in candidature for any other degree.

Professor A.K.M.Azharul Islam
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CANDIDATE

ABSTRACT

A theoretical analysis of the interionic potential in four rutile-type oxide crystals has been made within the framework of ionic model using eight repulsive interactions including one proposed in this work. The suitability of the new interaction potential as applied to these system is discussed. A new complete set of polarizability values of the ions concerned has also been derived. The lattice energy and pressure derivative of bulk moduli are evaluated for the entire family of crystals under study. The resulting values are compared with the available experimental data and other recent theoretical calculations.

We have also considered the question of the degree of ionicity of the compounds under study as there seems to be some controversy regarding these in literature. The present study indicates that the bonding in rutile is predominantly ionic, although some covalent contribution is present.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 General Introduction :

A solid has an arrangement of atoms (or molecules) in which the atoms are arranged in some regular repetitious pattern in three dimensions. It can be classified according to a variety of criteria. Among the more significant of these is the description of a solid as being neither crystalline or amorphous. The sample of macroscopic crystalline solids have been chosen by chemists and physicists for studying the structures of matters, interatomic bonding and other related chemical properties on an atomic scale. All of the mechanisms which cause bonding between atoms derive from electrical attraction and repulsion. The differing strengths and differing types of bond are determined by the particular electronic structures of the atoms involved. The weak van der Waals(or residual) bond provides a universal weak attraction between closely spaced atoms and its influence is overridden when the conditions necessary for ionic, covalent or metallic bonding are also present.

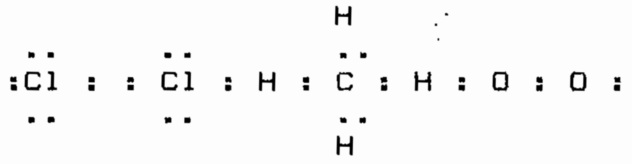
An ionic bond may be thought of as the result of the complete transfer of an electron from one atom to another. The alkali halides such as NaCl are typical members of the class of ionic solids. NaCl crystallizes as $Na^+ Cl^-$. The alkali metals such as sodium have a single valence electron outside a closed shell. Where as halogens such as chlorine are one electron short of having a complete outer shell. An electron transfer from the alkali metal X to the halogen Y will result in closed shells for both X^+ and Y^- ions .This happens in a salt XY. For example in NaCl, Na has an electronic configuration $1s^2 2s^2 2p^6$ which is the same as that of neon, whereas Cl has $1s^2 2s^2 2p^6 3s^2 3p^6$ which is the same as that of argon. Since these electronic configurations are very stable, it can be said that an ionic crystal consists of positive and negative ions. Besides alkali halides, ionic crystals can also be made of divalent and trivalent atoms for example CaO, $MgCl_3$, Al_2O_3, Na_2S and ZnO etc.

Ions have the same electronic structure as the nearest inert gas atoms except that they are electrically charged. This charge is spherically distributed and represents the difference between the charge on the nucleus and the sum of the electronic charge surrounding it. When oppositely charged ions are brought together each ion tends to neutralize its charge by surrounding itself with ions having an opposite charge. Because ions having like charges repel each other, the stable packing attained is determined by the relative sizes of the ions and their respective charges. A periodic array therefore results in which the environment of all similar atoms is the same and the sum of all positive and negetive charges and upto zero so that the ionic solid is electrically neutral.

Ionic bond is fairly strong as known from the amount of work required to dissociate an ionic solid into its components. Binding energy of NaCl is 7.8 ev and binding energy of LiF is 10.4 ev. This strong binding means that ionic crystals are hard and have relatively high melting and boiling points. Normally they are transparent to visible light while they exhibit a single characteristic optical reflection peak in the infrared region. Crystals are quite soluble in ionizing solvents such as water, the solutions being highly dissociated with free ions. The valence electrons are also bound quite tightly to ionic nuclei so that electrical conductivity via electrons is not possible and ionic crystals are insulators at room temperature. At high temperatures ions themselves become more and more mobile and ionic conductivity become possible.

As a consequence of the spherical charge distribution ionic bond is non-directional. For special cases, ionic bonds have some directional characters. Ionic crystals usually crystallize in the relatively closed packed NaCl and CsCl structure.

In covalent bond two electrons become shared between the atoms which are being joined. The covalent bond, sometime referred to as a valence or homopolar bond, is an electron pair bond. The result of this sharing is that the electron charge density is high in the region between the two atoms. The hydrogen molecule, H_2serves as a simple example of the covalent bond. The other examples of covalent bond:



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\;:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\quad H:\overset{H}{\overset{\cdot\cdot}{\underset{\underset{H}{\cdot\cdot}}{C}}}:H\quad :O:O:$$

The dots between the atoms indicate the electron pair bond.

<u>Characteristics of a Covalent bond</u>:

1.Covalent bond has a saturation property. Let us consider the interaction of a hydrogen atom with a helium atom. An exchange of electrons between H and He with parallel spins result in repulsion, whereas an exchange with antiparallel spins violates the Pauli exclusion principle. Therefore, covalent bonding exists only between atoms with unpaired spins. For example in CH_4 for carbon to have unpaired spins, the four valence electrons must have the configuration $2s\ 2p^3$ in contrast to the ground state configuration $2s^2\ 2p^2$. The four orbital wave functions are mixtures of the one 2s and three 2p wave functions called the sp^3 hybrid orbital and they have electron distributions directed towards the four corners of a tetrahedron. Typical examples of crystals with nearly pure covalent bonds are diamond, silicon and germaniun.

2. Covalent bonds are strongly directional in character i.e. the electrons tend to be concentrated along the lines joining the adjacent atoms.

3. Covalent crystals are usually hard brittle with quite high binding energies and thus have high melting and boiling points.

4. They are transparent to long wavelengths but opaque to shorter wavelength, the transition is abrupt and occur at a characteristic wavelength usually in the visible or infrared.

5. Covalent crystals are typical semiconductors whose electrical conductivity is quite sensitive to impurity

and change of temperature. In molecular crystals binding arises solely from dipolar forces between the atoms or molecules of the crystal. Even when an atom or molecule has no average dipole moment it will in general have instantaneous fluctuating dipole moment arising from instantaneous positions of the electrons in their orbitals. For example Germanium. Here unpair bonds exist at the boundary of the structure. These unpaired bonds are generally referred to as dangling bonds and they are responsible for the fact that germanium and silicon surfaces are quite active chemically.

Covalent binding is all that is needed for Ge atoms to form a germanium crystal. This is not the case with CH_4 . The bonds in $CH_4$are all used up. Thus no additional bond pairs can be formed with neighbouring CH_4molecules. The binding between such molecules comes from binding force arising from fluctuating dipole interaction called as van der Waals forces. It turns out that an atom or a molecule is polarizable not only under an external electric field but under the field of other atoms or molecule as well. As a result a very small electric dipole develops.

The instantenuous dipole moment is the source of an electrostatic dipole field which in turn may induce a dipole moment in other atom or molecule. The interaction between the original and induced dipole moment is attractive and can serve to bind a crystal in the absence of ionic or covalent binding. Binding forces are usually quite weak, the binding energy due to them falls off as 1/r where r is the distance between the dipoles .

Molecular crystals have small binding energy and consequently have low melting and boiling points. They are usually poor electrical conductors. Crystals of organic compounds are usually of this type as are the inert gases He ,Ne , A etc. in the solid state.

In metallic crystals free electrons are present. The outstanding characteristic of a metal is its high electrical conductivity.

The fig 1-[illegible] shows the wave function of the valence electron in a sodium crystal indicated by solid line as compared to 3s wave function of a sodium atom indicated by dashed line. The wave function is not disturbed near the ion core but in the outer region it is considerably flattened and squcezed in by neighbouring valence electrons. Since the distribution of electrons in volume element $4\pi r^2 dr$ is given by $|\psi|^2 4\pi r^2 dr$ over 90% of the electron distribution is in this flat re-

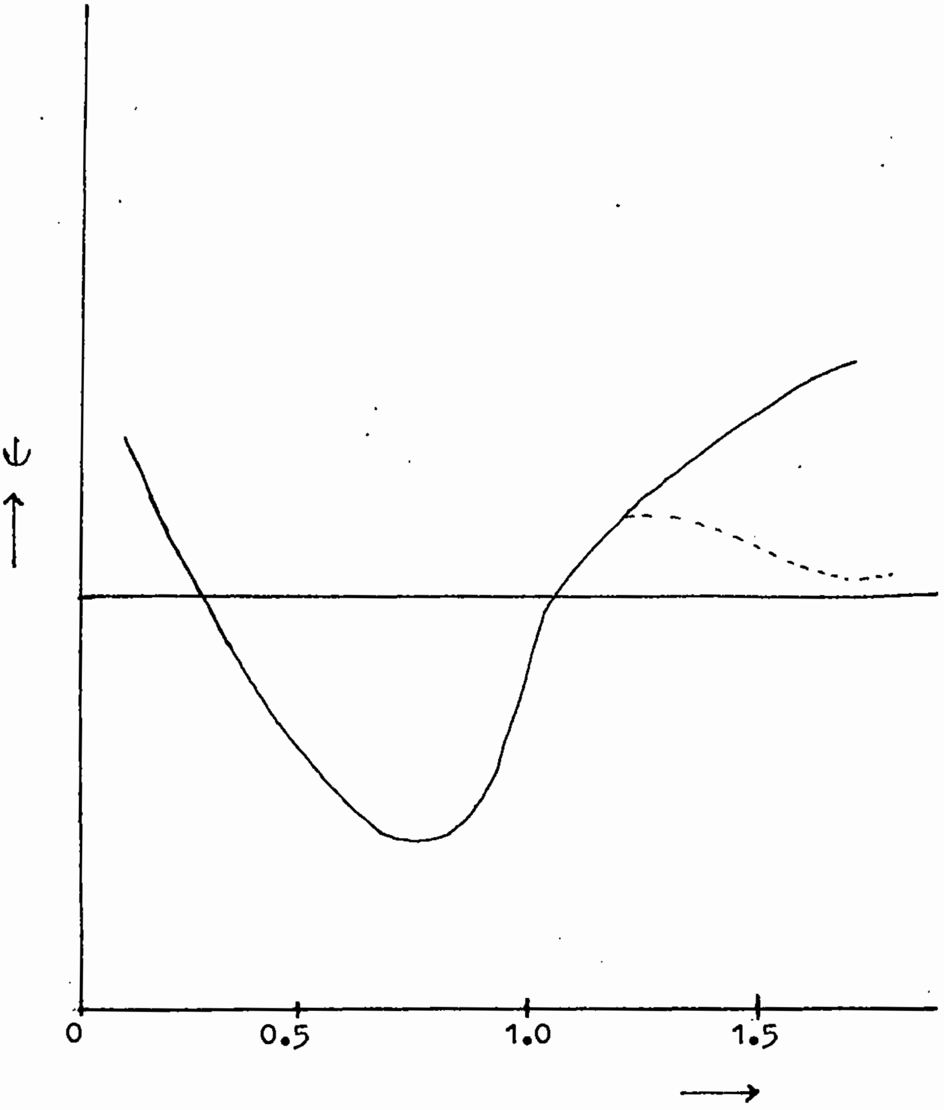


Fig. 1-o : Wave function of valence electrons 3 S wave function (theoretical)

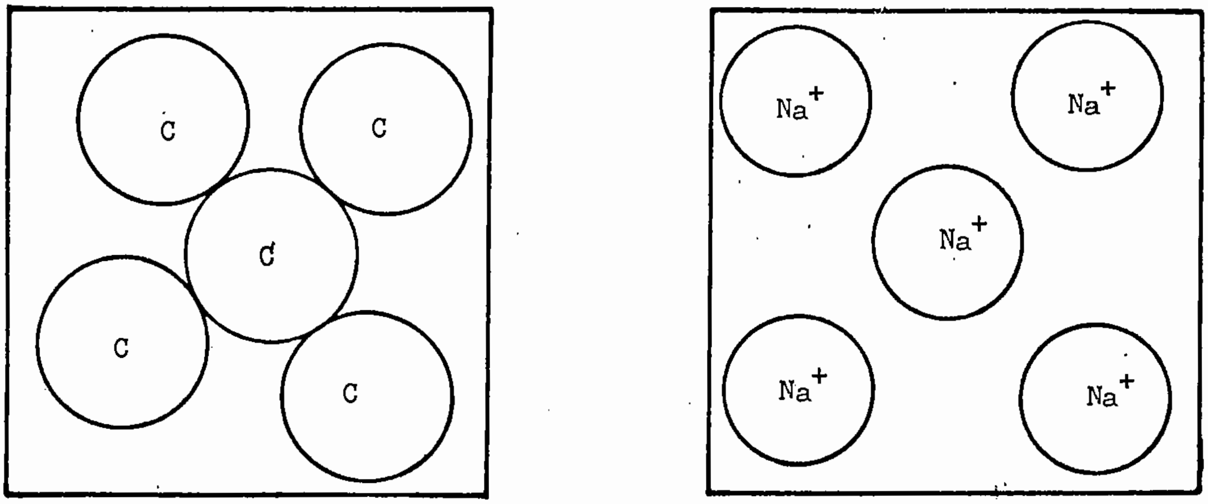
gion. The potential energy of the electron is obviously lowered because the average electron distribution is now close to the nucleus. The kinetic energy being proportional to $\{\frac{h}{2\pi}\frac{d\psi}{dr}\}$ is also reduced because of a smaller $\frac{d\psi}{dr}$ in the flattened region. The reduction in the total energy constituted a bond between atoms in a metallic crystal.

In the case of metallic sodium the situation is changed for two essential reasons.

(i) First, each sodium atom has eight nearest neighbours in a body centred cubic structure. Therefore on the average, each atom forms only one eighth of an electron pair bond with one particular neighbour.

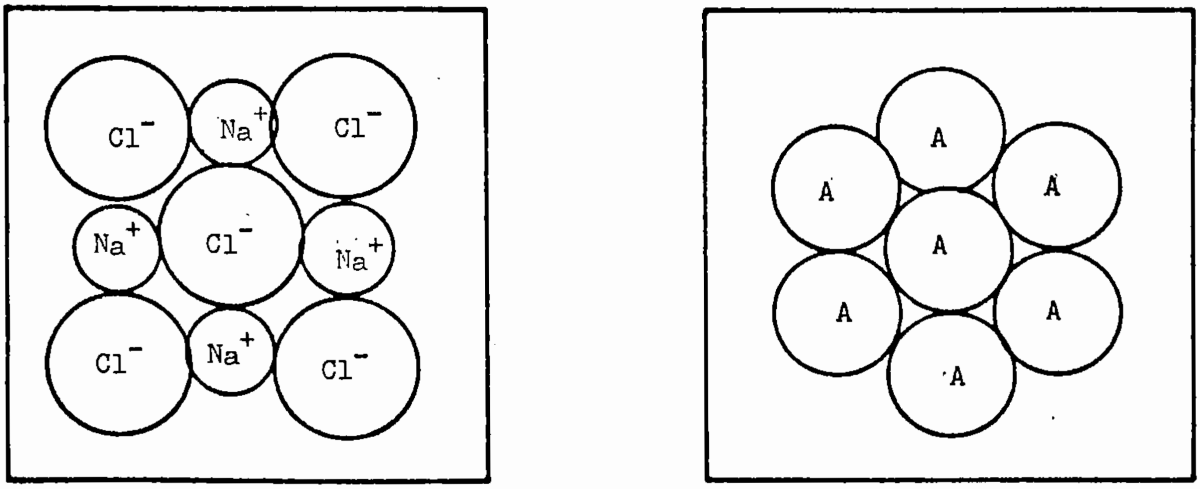
(ii) Secondly, as a result of electrostatic interactions the energy levels of the atom broaden out to form a bond as the interatomic distance decreases.

The number of quantum states in each bond is exactly equal to the number of atomic states multiplied by the number of atoms involved. If the model of covalent binding is adopted we see that quantum states are now available to the third sodium atom. From the view point of covalent bond the metallic bond is unsaturated one and hence there is no contradiction between the two view points.



(a) Diamond (covalent)

(b) Sodium (metallic)



(c) Sodium chloride
(ionic)

(d) Crystalline (argon
(van der Waals)

Fig : 1-1 :The Principal types of crystalline bonding forces.

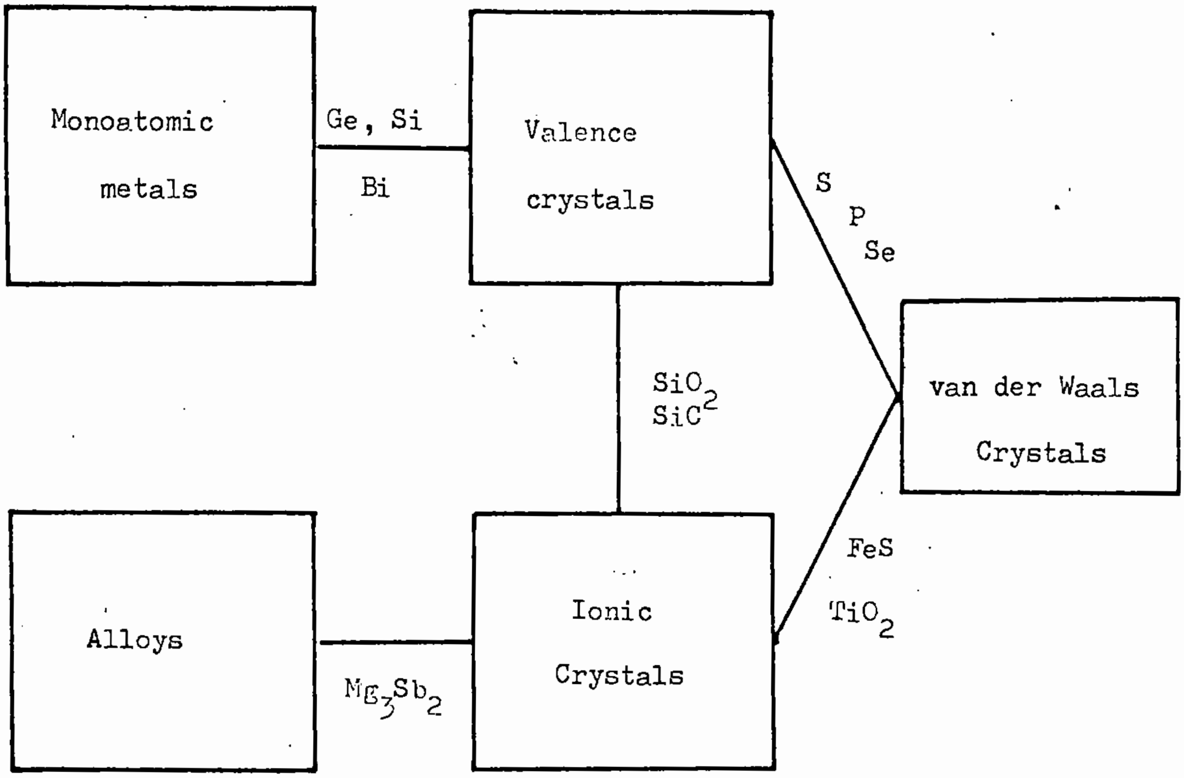


Fig. 1-2 : Classification of solids , Indicating intermediate cases.

The transitions between crystal types is not sharp at all, e.g. tin can exist in two crystal forms one being metallic and the other covalent.

It should also be noticed that all semiconductors are not covalently bound. Crystals such as CuO, ZnO and CdS are more ionic than covalent but they have also energy bands as also Ge and Si when sufficient electrons are in the upper bond these will behave like semiconductors. Other examples of transition cases include some metal alloys such as Mg , Sb Zn and As which can be considered partly metallic and partly ionic and some molecular crystals such as S and P are partly molecular and partly covalent.

Metallic crystals have high electrical and thermal conductivity. They have high optical reflection and absorption co-efficients. The binding energy of ideal metals such as alkali metals arise from the interaction of the free electron gas.

Hydrogen bond is formed by a hydrogen ion located between two anions. Since hydrogen has only one electron it can lose it to either of the two adjoining ions with the result that there is an equal probability of finding the electron on either ion. The positive hydrogen ion tends to draw the two anions more closely together than their normal seperation in crystals so that such a shortering of their interatomic seperation serves to indicate the presence of a hydrogen bond. It is noticed that the hydrogen bond is largely ionic in character being formed only between the most electronegative atoms, particularly F, O, and N. In the extreme ionic form of the hydrogen bond the hydrogen atom loses its electron to another atom in the molecule; the bare proton forms the hydrogen bond.

Crystal structure :

The study of the physical properties of the solid state began in the early years of this century. A century ago the study of crystals was concerned only with their external form and with symmetry relationships among the various co-efficients that describe the physical properties. All atoms are constructed of various elementary particles (electrons, protons, nuetron etc) and a complete description of a solid would simultaneously specify the condition of all these particles. The solids have an arrangement of atoms (or molecules)in which the atoms are arranged in some regular repetitious pattern in three dimensions. Such solids are called crystals and the arrangement of atoms is termed the crystal structure. The logical relation for crystal structure is,

$$\text{Lattice + basis = crystal structure.}$$

Where a lattice is a regular periodic arrangement of points in space. A lattice is a mathematical abstraction; the crystal structure is formed only when a basis of atom is attached identically to each lattice point. The set of points r' specified by $r' = r + n_1 a + n_2 b + n_3 c$ for all values of the integers n_1, n_2, n_3 defines a lattice. The structure of all crystals in terms of a single periodic lattice, but with a group of atoms attached to each lattice point. This group of atoms is called the basis; the basis is repeated in space to form the crystal.

A typical structure of simple ionic solid is illustrated in fig.1-3 to 1-6. The structure is composed of a number of interpenetrating simple cubic or face-centered cubic Bravais lattices. With reference to the cube axes, the CsCl structure is composed of two sc lattices, one for each species of ions, shifted by a $\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ relative to one another, while the NaCl structure and the Zinc blende structure are composed of two fcc lattices, shifted by $\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ and $\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ respectively. Similarly, the CaF structure is composed of three fcc lattices, one for one species of ions and two for the other species, shifted with respect to the former by $\{\frac{1}{4},\frac{1}{4},\frac{1}{4}\}$ and $\{\frac{3}{4},\frac{3}{4},\frac{3}{4}\}$. Finally, the Cu_2O structure is composed of six sc lattices, two for one species of ions, with their origins at $\{\frac{1}{4},\frac{1}{4},\frac{1}{4}\}$ and $\{\frac{3}{4},\frac{3}{4},\frac{3}{4}\}$ and four for the other species, with their origins at $\{0,0,0\}$, $\{\frac{1}{2},\frac{1}{2},\frac{1}{2}\}$, $\{\frac{1}{2},0,\frac{1}{2}\}$, $\{0,\frac{1}{2},\frac{1}{2}\}$. The unit cell of stoichiometric rutile is tetragonal and contains six ions per unit cell as shown in fig.(1-5). The crystals have the space-group $p\,\frac{4_2}{m}\,\frac{2_1}{n}\,\frac{2}{m}$ with $Z=2$, the cations occupy equivalent position 2{a} at {0,0,0} and $\{\frac{1}{2},\frac{1}{2},\frac{1}{2}\}$ with site symmetry m m m, the anions reside in 4(f) at$\frac{1}{2}$((X,X,0),1/2+X,1/2−X,1/2}, with symmetry mm.

The existence of a stable bonding arrangement implies that the spatial configuration of positive ion cores and outer electrons has less total energy than any other configuration. The energy deficit of the configuration compared with isolated atoms is known as the cohesive energy and ranges in value from 0.1 ev atom for solids which can muster only the weak van der Waals bond to 7ev/atom or more in some covalent and ionic compounds and some metals. The cohesive energy constitute the reduction in potential energy of the bonded system minus the additional kinetic energy which the Heisenberg uncertainty principle tells us must re-

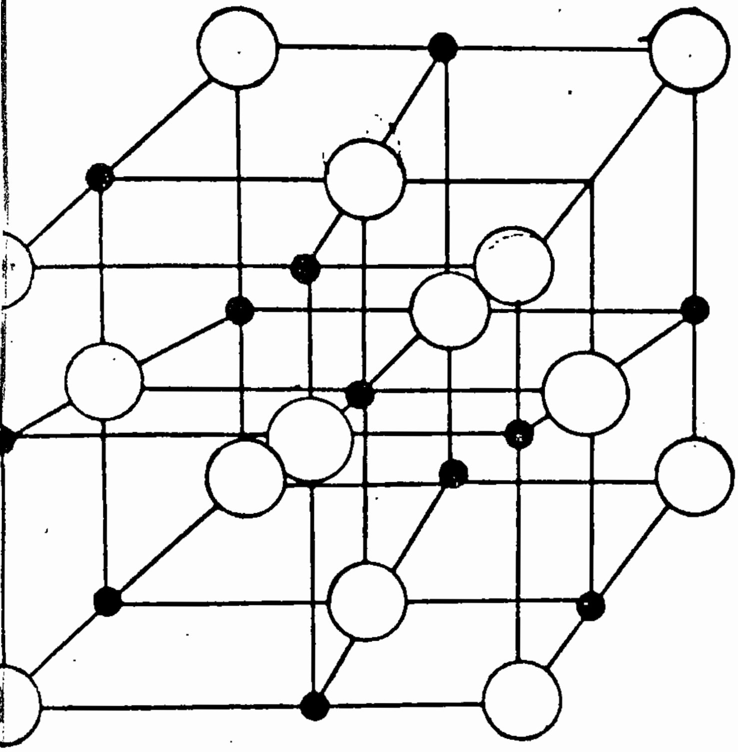


Fig. 1-3 : A lattice cell of sodium cloride structure.

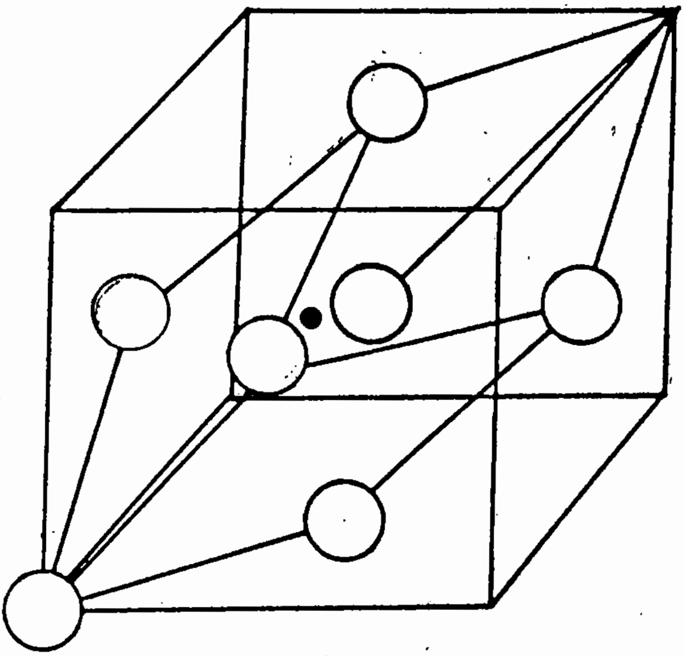


Fig. 1-4 : A unit cell of sodium cliride structure.

○ → Cl^-

● → Na^+

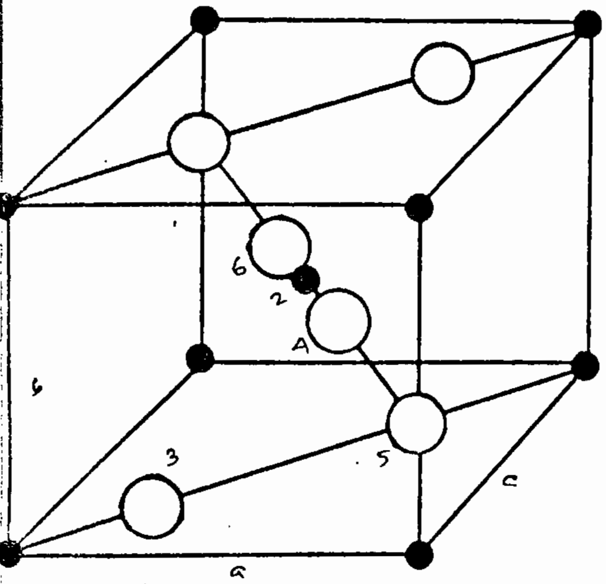


Fig. 1-5 : A lattice cell of rutile structure.

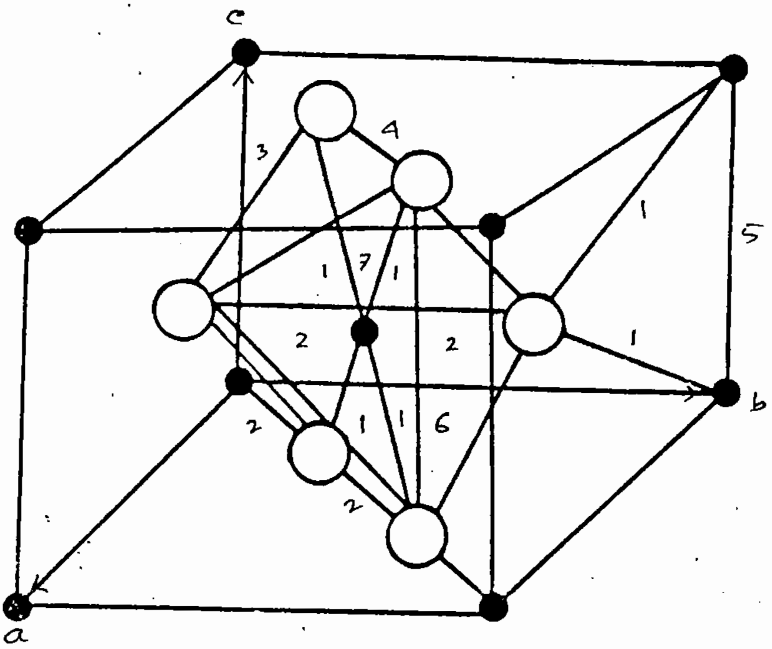


Fig. 1-6 : A unit cell of rutile structure.

● → X

○ → Y

sult from localization of the nuclei and outer shell electrons. It shall now be considered the forces which holds the atoms or constituent particles together in a crystalline solid. These forces or bonds are of prime important in understanding differences in the gross structures and characteristic of different solids. Since atoms contain charge particles, they exert forces on each other when brought together. It is due to the influence of these interatomic forces that the constituent particles of a crystal obtain the position corresponding to a minimum energy configuration and thus get bonded together. These interatomic forces were first observed in the field of crystal chemistry dims studies on the composition and stabilization of molecules. It is significant to note that investigations of the nature and origin of the interatomic forces did not await the development of X-ray diffraction and crystal structure analysis techniques. Around the mideighteenth century, Desaguliers suggested that these forces were of an electrical nature. This theory was further improved upon by Berzellius in the early ninteenth century. The development of Bohr's theory on atomic structure in 1913 provided the physical basis for the interpretation of the interatomic forces. The discovery of X-ray diffraction and the subsequent advances in crystal structure analysis provided the necessary means to find out the atomic configuration of molecules whose forms were previously conjectured on the basis of valency theories of chemistry. One significant fact that which emerged from the earlist analysis of the structure of crystals was that no essential distinction existed between the chemical forces which bound the atoms of the chemical molecules and the physical forces which held together the atoms in a crystal. This important finding was significant in two ways. First, it provided physicists with the means to explore the nature of the forces which bound the atoms in crystals by utilizing ideas from chemistry and suitably extending them. Secondly, it opened a way to the physical interpretation of the concent of chemical bonds pioneered by chemists.. For the present purpose one shall be concerned with the first of the two aspects. The direct analogy which exists between the two forces also makes it evident as to why one classify the discussion on the bonding of atoms in crystals as chemical bonding.

Next we turn our attaintion to discuss ionic crystals. The nature of binding in ionic crystals have been a subject of extensive study over the past few decades [1-11]. These studies have been made possible accurate study on the investigation of the nature of the bonds, cohesive energy and other related chemical properties. A number of attempts have been made to approximate the interionic potential in such crystals by assuming them to be composed of completely ionized atoms, and earlier models along these lines have been proposed by Born and Lande [1], Born and Mayer [2],Rittner [3], Varshni and Shukla[4] and Patel et. al.[5]. These evidences have been accepted as being reasonably successful in describing the ionic bond in diatomic, ionic molecules and crystals. Reviews of the progress in this field have been made by Sherman[6],Waddington[7], Ladd and Lee[8]. The improved in recent years has made possible study of bonding and other related chemical properties in ionic molecules and crystals by Kachhava and Saxena[9], Mathur and Singh[10], Pandey [11], Pandey and Saxena[12], Barr and Lidiard [13] and Redington[14].

Recently Ch.Satyanarayan[15] studied the static properties and stability of structure of ammonium halides. Ammonium halides are diamorphic, crystallizing in the CsCl-type crystal. Structure at low temperature and in the NaCl-type crystal structure at high temperature with the exception of NH_4F which crystallizes in the Wurtzite-type lattices[16]. A predominantly ionic character of binding in ammonium halides[17,18] , motivated the recent researchers to concentrate on the studies of their static and dynamic properties. Bleick[16] comput the cohesive energies of ammonium halides. The van der Waals terms were computed by using London Margena(LM) formulas. But these formulas have been criticized because they are subject to considerable uncertainties. Attempts to compute the cohesive energies have been made by Ladd and Lee[19] ; by Murthy et. al.17]. and by Singh et. al.18] with varying degrees of success.

In recent years, a large number of potential energy functions have been applied to study the various thermodynamic properties of alkali halides, by Cubicciotti[20] , Sharma and Madan[21] ,Kachhava[22],Mishra and Sharma [23] and Sharma and Tripathi[24]. J.Shanker and G.D.Jain[25] have devloped an interionic force model for mixed alkali halide crystals. Using empirical Born and Mayer exponential form. But it has some shortcommings in describing various properties. Therefore, Harrrison [26] has presented a quantum mechanical treatment to calculate the cohesive energy and bulk modulus at NaCl - NaBr, KCl-KB and KB-KI mixed crystals.

Studies on the alkali halides provide a critical test of different interionic potentials mainly because they exist or three different states viz. (i) molten states (ii) crystalline state and (iii) molecular state. The B-M form on alkali halide can not explain the molecular properties of diatomic alkali halides [3, 27]. Woodcock [28] proposed a compoite form and applied in alkali halides molecules and crystals by calculating the binding energy and compressibility. This potential [28] has been also applied by Michielsen et. al. [29] in crystalline molecular and molten states . Some errors have been noticed in the treatment of Michielsen et.al. [29]. The errors are corrected by Woodcock[28].

An analysis of interionic potentials in CaF SrF and BaF crystals has been performed [30] by modifying the traditional Born model treatment. The cohesive energy, bulk modulus and its pressure derivative for alkaline earth fluoride crystals are calculated. The values are inconsistent in some cases. Alkali halides because of their wide-ranging importance as ionic crystals and molecules have been the subject of extensive studies. For the study of their structures and properties one generally prefer a model potential for them. These potentials are mainly based on electrostatic treatment of interionic interactions and are very simple and suitable for applications in various fields of physico chemical intercepts. With this view a large number of attempts [2,3,27,31-34] have been performed for ionic molecules. Excellent results of these potentials have been given by Varshni and Shukla [27], and by Das and Saxena [35].

More than twenty compounds crystallize with rutile structure (oxide crystals). The structure consists of a primitive tetragonel lattice with six atoms per unit cell and belongs to the space group D_{4}^{14} ($P^{4}2/mnm$). Such solids exhibit several unusual and interesting features [36] which deserve thorough investigation. Many physical properties of rutile-type compounds have been measured by Grants [37] and Rogers et. al. [38]. The rutile structure oxides with interesting dielectric, magnetic and chemical properties have thus been subjected to many investigations [1,2,28,39-46]. But the controversy about the degree of the ionic nature of these compounds has not yet been settled. Thus an attempt has been made for a thorough theoretical study of rutile structure oxides compounds in this thesis.

General introduction is discussed in chapter 1. Lattice energy and pressure derivative of Bulk moduli are described in chapter 2. The origin and different empirical forms for repulsive potential (from 1918-1985) are discussed in chapter 3. The origin of van der Waals energy and derivation of van der Waals coefficients are presented in chapter 4. The origin of polarizability,a discussion of polarizability versus ion environment and methods of calculating polarizability are also presented in chapter 4. The calculations and results are discussed in chapter 5. Chapter 6 contains a discussion and a conclusion of the results obtained where it is shown that relatively simple theory with a new RPE function is moderately successful in explaining the properties of crystals under study.

CHAPTER 2

LATTICE ENERGY AND PRESSURE DERIVATIVE OF BULK MODULI.

2.1 Introduction:

The attractive electrostatic interaction between the negative charges of the electrons and the positive charges of the nuclei is extremely responsible for the cohesion of solids. To understand cohesion one compare the total energy of the solid with the energy of the same number of free neutral atoms at infinite seperation. A crystal can only be stable if its total energy is lower than the total energy of the atoms or molecules when free. The difference (free atom energy)-(crystal energy) is defined as the lattice energy.

The total energy per molecule of a crystal relative to infinite separated ions is

$$U_T = U_{LR}^{C} + U_{SR}^{R} + U_{SR}^{vdW} + U_{ZP} \qquad (2-1)$$

where U_{LR}^{C}= Long-range coulomb potential.

$U_{SR} = U_{SR}^{R} + U_{SR}^{vdW}$

U_{SR}^{R} = short-range repulsive potential.

U_{SR}^{vdW}= short-range van der Waals energy.

U_{ZP} = Zero-point energy.

A. Long-range Coulomb energy (U_{LR}^{C}):

The Coulomb interaction energy of point like charges Z_{pe} and Z_{pe} pertaining to the pth ion in the lth unit cell and to the p′th ion in the reference cell is $Z_p\ Z_p\ e^2/\ (r_l + r_p - r_p)$. The corresponding electrostatic energy of the crystal per molecule is then given by

$$U_{LR}^{C} = (2n)^{-1} \sum_{l}{}^{\prime} \sum_{p,p} Z_p\ Z_p\ e^2/\ (r_l + r_p - r_p) \qquad (2\text{-}2)$$

where the superscript in the summation indicates that the case l = 0 is excluded for p = p′, and n is the number of molecules in the unit cell. Equation (2-2) can be rewritten in the form :

$$U_{LR}^{C} = -(Z\ e)^2 \alpha_R / R \qquad (2\text{-}3)$$

where , Z is the largest common factor of the Z_p′ s and R is a characteristic length of the crystal structure. The additional quantity α_R the Madelung constant reffered to the characteristic lenght R is defined as

$$\alpha_R = -\frac{R}{2n} \sum_p \varphi_p\, \psi\,(r_p) \qquad (2\text{-}4)$$

Here $\varphi_p = Z_p / Z$ and

$$R\,\psi\,(r_p) = \sum_l \sum_p \frac{\varphi_p}{|(r_l + r_p - r_p)|/R} \qquad (2\text{-}5)$$

is the electrostatic self potential of the crystal at the lattice point r when the ionic charges are measured in units of Z e and the interionic distances in units of R. The Madelung constant is clearly independent of the absolute value of the ionic charges and of the absolute value of the cell edges; it depends only on the crystal structure.

B. Evaluation of Madelung constant:

The Coulomb energy constant α was made by Madelung [47]. The general method for lattice sum calculations was developed by Ewald[48]and Evjen and Frank[49] have given simple methods which arrange the counting in rapidly convergent ways.

The Madelung constant is defined as:

$$\alpha = \sum_{j}{}' \frac{(\pm)}{p_{ij}} \qquad (2\text{-}6)$$

where p_{ij} is the quantity difined by the relation $r_{ij} = p_{ij}$ R where R is the nearest neighbour seperation in the crystal. If one takes the reference ion as a negative charge the plus sign will be used for positive ions and the negative sign for negative ions. An equivalent definition is

$$\frac{\alpha}{R} = \sum_{j}{}' \frac{(\pm)}{r_j} \qquad (2\text{-}7)$$

where r_j is the distance of the jth ion from the reference ion and R is the nearest-neighbour distance.

For example one picks a negative ion as reference ion, and let R denote the distance between adjacent ions. Then

$$\frac{\alpha}{R} = 2\left(\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \cdots\cdots \right) \qquad (2\text{-}8)$$

Na^+ ion at arbitrary zero position

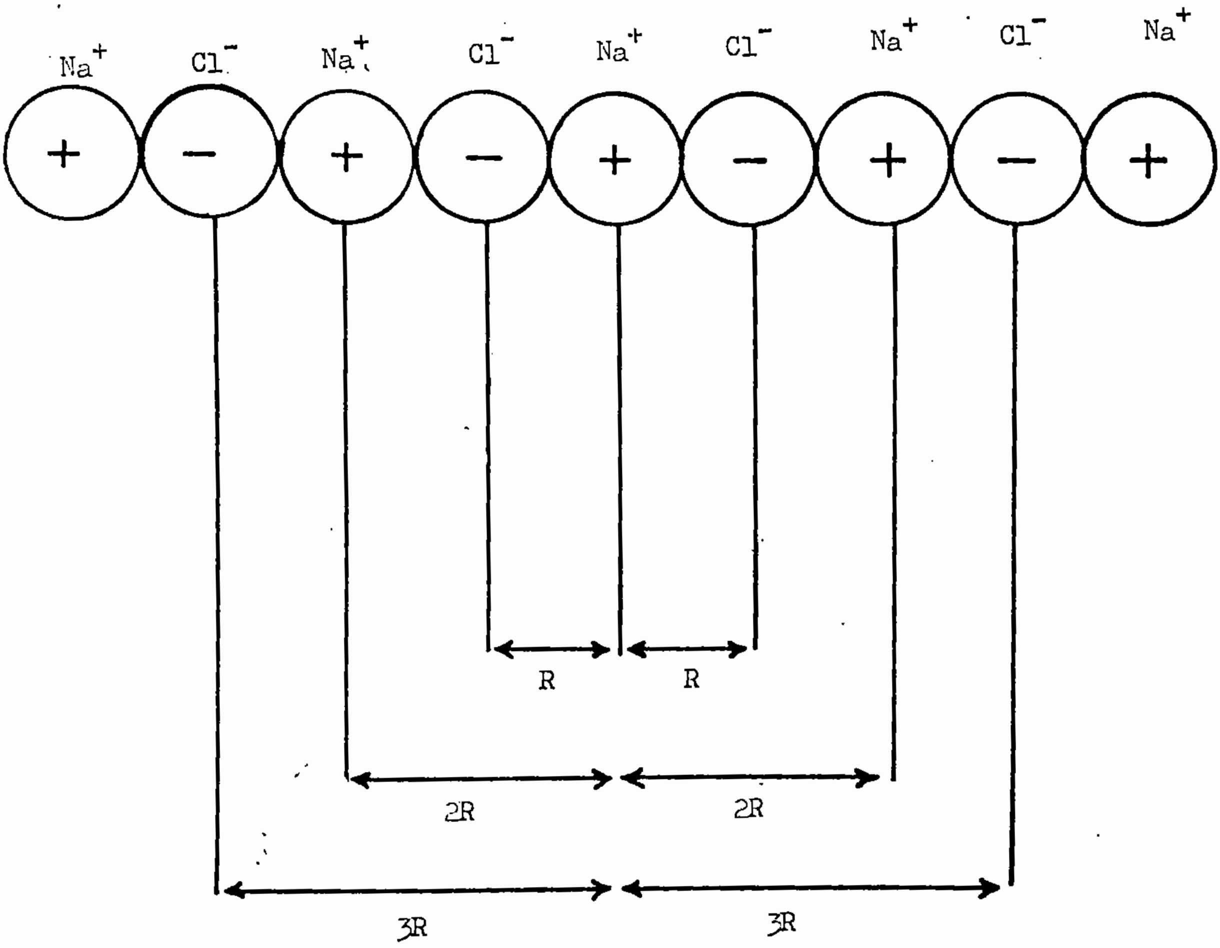


Fig. 2- 1 : One dimensional approximation to the NaCl structure.

the factor 2 occurs because there are two ions, one to the right and one to the left, at equal distance r_j. One sums this series by the expansion

$$\log (1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + ...$$

Thus for the one-dimensional chain the Madelung constant $\alpha = 2\log 2$.

C. Repulsive energy:

The equilibrium conditions for a solid can be satisfied only if the interatomic forces become repulsive at small interatomic distances. The short-range repulsion between atoms is connected with the role of the exclusion principle in opposing overlap of closed electron shells. This is explained simply in the case of two hydrogen atoms with parallel electron spins in their ground state by the comparison between the energy of the triplet state of the molecule computed by first order perturbation theory and the corresponding pseudoclassical energy. These are given respectively[50] by the mean value of the molecular Hamiltonian over the antisymmetrized product of hydrozen 1s wave functions and by the mean value of the molecular 1s wave functios,

$$U_{SR}^{R}(r) = 2U_H + \frac{e^2}{a_H} e^{-2r/a_H}\left(\frac{a_H}{r} + \frac{5}{8} - \frac{3}{4}\frac{r}{a_H} - \frac{1}{6}(r/a_H)^2\right) \quad (2-9)$$

Here U_H is the energy of the hydrogen atom in its ground state, r is the interatomic distance and a_H is the first Bohr radius. It is showed clearly that the repulsion is due largely to effects which are neglected in the pesudoclassical calculation. It is also seen that the repulsive energy of equation (2-9) in the range of large interatomic distance where this first order perturbation expression applies, decays almost exponentially with incresing interatomic distance, although with a logarithmic rate smaller than ($\frac{a_H}{2}$ $)^{-1}$. The analogous problem of the interaction between two hydrogen like ions, of not charge $Z_1 e$ and $Z_2 e$, has been worked out by Pauling[51] in the same approximation. The resulting formula for the energy of the triplet state of the molecule involves, besides the Coulomb interaction energy of the net ionic charges, the repulsive energy of equation (2-9) multiplied by a factor approximately equal to $1 + Z_1 + Z_2$.

Further discussion about repulsive energy and its different empirical forms are presented in details in chapter 3.

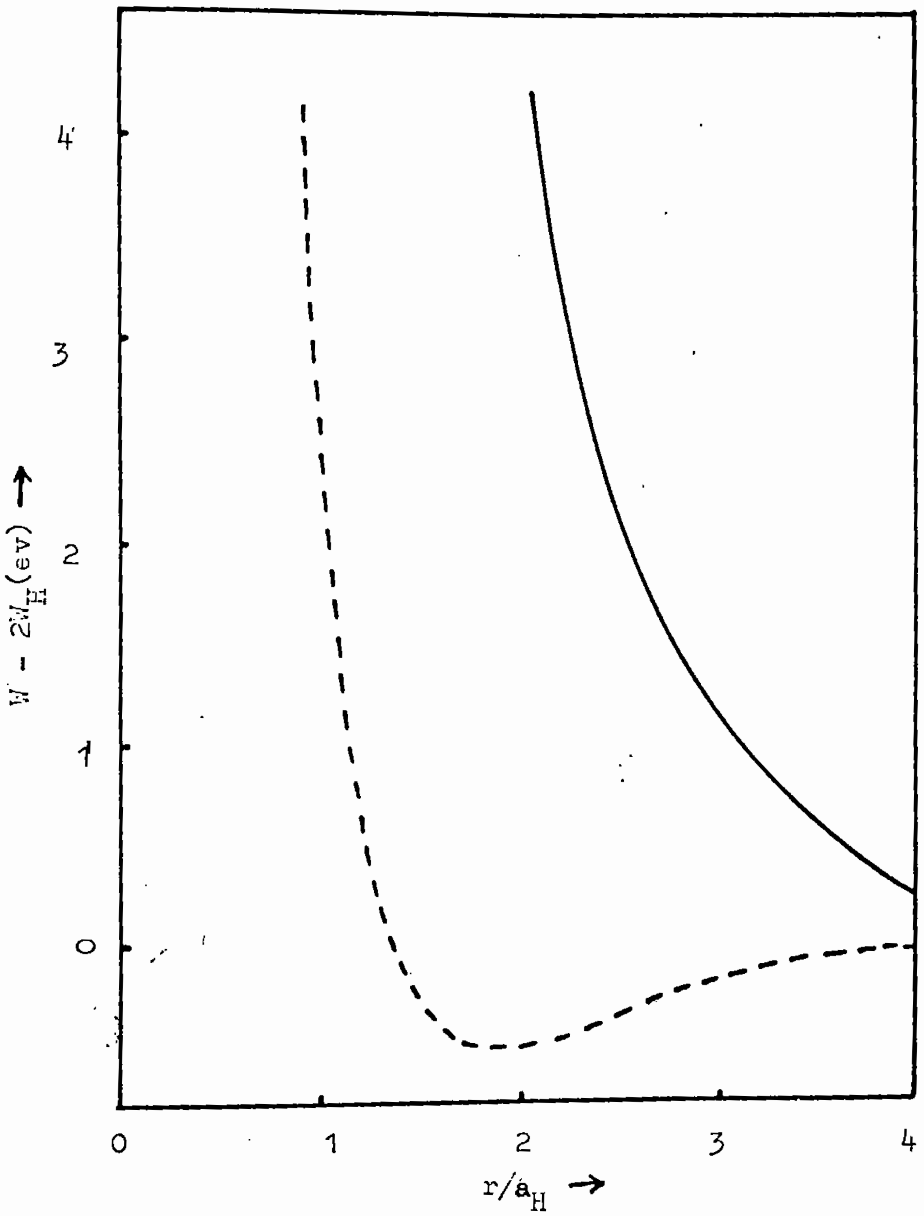


Fig. 2-2 : Interaction energy of the two hydrozen atoms with parallel electron spin in their ground state. The solid curves gives the anergy of the triplet state of the molecule and dashed curve gives the pseudoclassical interaction energy.

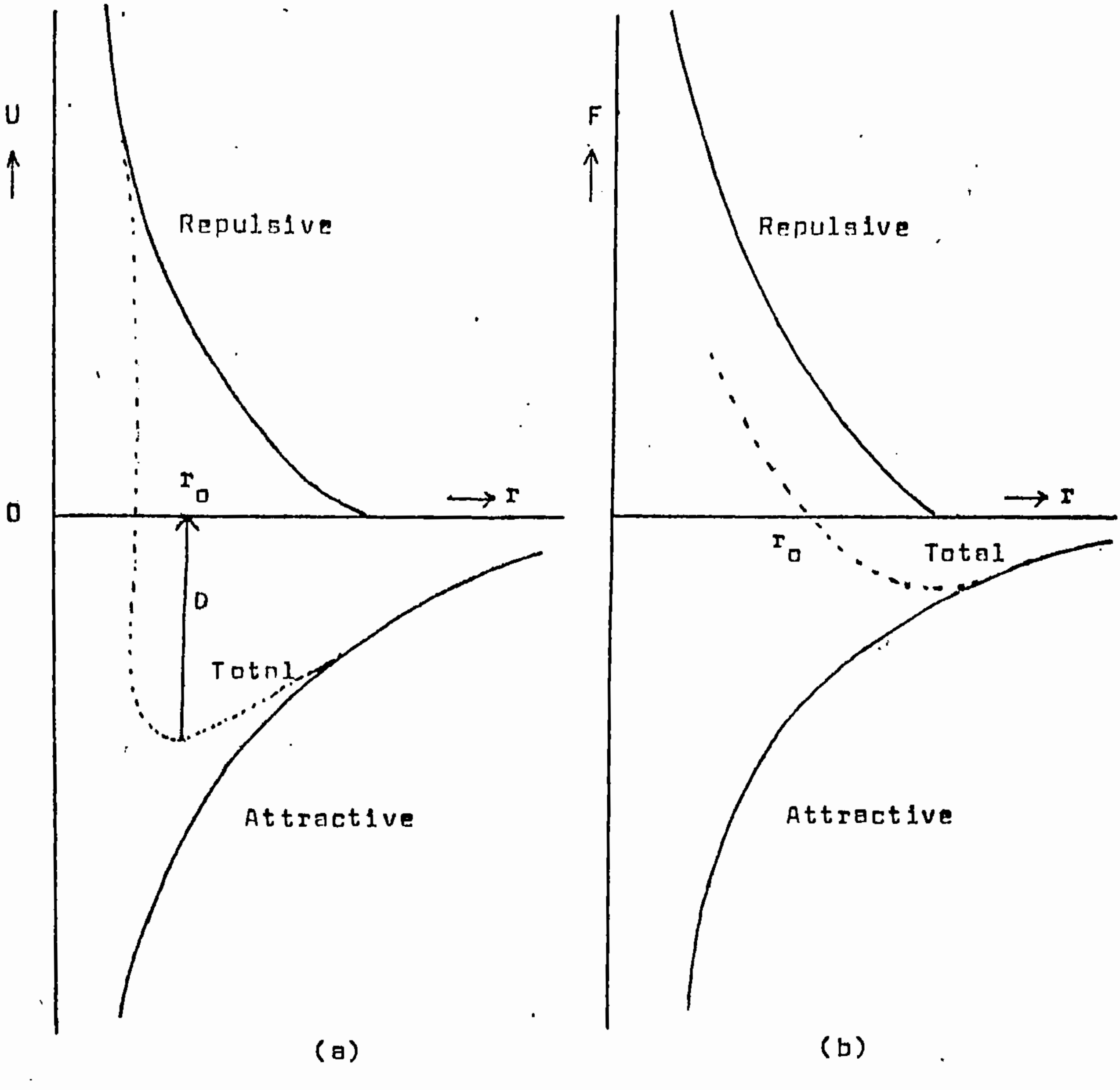


Fig. 2-3 : Schematic representation of the energy (a) and force (b) between two atoms as function of their separation r. The dashed curves are the sums of the attractive and repulsive curves.

D. van der Waals energy:

The existence of condensed phases for the rare gas elements shows that there are attractive interactions between closed shell atoms which are of a different nature from the Coulomb interactions between ions and from the overlap attractive interactions. The physical origin of these so called van der Waals forces is connected with correlations of the electronic motions in different atoms and can actually be understood in semiclassical terms[52]. Indeed, the instantanuous dipole moment μ of a closed shell atom induces on a similar atom a distance r away a dipole moment, which is proportional to $\frac{\alpha\mu}{r^3}$ where α is the atomic polarizability and produces at the location of the first atom a field proportional to $\frac{\alpha\mu}{r^6}$. The related term in the interaction energy is thus of the form $-\alpha\bar{\mu}^2/r^6$ where $\bar{\mu}$ is the mean dipole moment of the first atom. In addition to such a dipole-dipole energy term, the consideration of the instanteneous higher moment of the charge distribution of the atoms yields other attractive terms, which decay more rapidly with increasing interatomic seperation. The actual evaluation of the van der Waals energy in a solid is unfortunately subject to considerable uncertainties. However, this is only a minor part of the cohesive energy of an ionic solid in standard thermodynamic conditions and possible errors in its value are largely compensated in a Born model treatment in the fitting of the parameter entering the overlap repulsive energy. The detailed of the van der Waals energy are described in chapter 4

E. Zero point energy:

A great step forward toward an understanding of the specific heat curves at low temperatures was made by Einstein[53] in 1906. For the average energy of an osillator Einstein made use of a result obtained by Planck in 1900, in connection with the theory of black-body radiation. According to Planck, a harmonic oscillator does not have a continuous energy spectrum as assumed in the classical theory, but can accept only energy values equal to an integer times h , where h is Planck's constant. The possible energy levels of a harmonic oscillator are given quantum mechanically by:

$$e_n = (n + \frac{1}{2})\, h\nu \quad \text{where} \quad n = 0,1,2 \qquad (2\text{-}10)$$

This has the effect of shifting all energy levels by the constant amount $h\nu/2$ and instead of Planck's average energy of an oscillator shown in the Fig. 2-3 at a temperature T, one obtains

$$(e) = \frac{h\nu}{2} + \frac{h\nu}{e^{h/KT}-1} \qquad (2\text{-}11)$$

The first term is called the zero-point energy of the osicillator because $(e) = \frac{h\nu}{2}$ for $T=0$. Now in the Debye theory of the specific heat of solids, a crystal is represented formally by a system of harmonic oscillators with a frequency spectrum given by:

$$F(\nu)\,d\nu = 4\,V\left(\frac{2}{C_t^3} + \frac{1}{C_l^3}\right)\nu^2\,d\nu \qquad (2\text{-}12)$$

where v is the volume of the crystal and C_t and C_l are, respectively the velocities of propagation of transverse and of longitudinal elastic waves. Making use of the definition of the Debye frequency ν_D. One may write

$$F(\nu)\;d\nu = \left(\frac{9N}{\nu_D^3}\right)\nu^2\,d\nu \qquad (2\text{-}13)$$

where N stands for the total number of atoms or ions in the crystal. Hence, at absolute zero, the contribution of the zero-point energy is

$$\frac{1}{2}\int_0^{\nu_D} F(\nu)\,h\nu\,d\nu = 9/8Nh\nu_D \qquad (2\text{-}14)$$

per ion pair, this corresponds to $9h\nu_D/4$. With a Debye frequency of the order of $10^{12}-10^{13}\,\text{sec}^{-1}$ this gives about 0.1 ev. As a correction to the lattice energy the zero-point energy, this contributes about 1 percent. The zero-point energy is very important for light elements (high Debye frequency).

2.2 Pressure derivative of bulk modulus:

In order to evaluate the pressure derivative of bulk modulus let us first censider the definition of bulk modulus. The bulk modulus B defined as:

$$B = - V \frac{dp}{dv} \qquad (2-15)$$

Neglecting thermal effects, from the first law of thermodynamics one may write,

$$dU = - pdV \qquad (2-16)$$

$$\text{or} \qquad \frac{dp}{dv} = - \frac{d^2U}{dv^2} \qquad (2-17)$$

$$\text{Therefore} \quad B = V \frac{d^2 U}{dv^2} \qquad (2-18)$$

It is well known to all $V = 2NR^3$ as volume per molecule is $\frac{1}{4}a^3$ and a= 2R. Where N is the total number of molecules and R is the nearest neighbour distance. Thus one may write

$$\frac{dU}{dV} = \left(\frac{dU}{dR}\right) \left(\frac{dR}{dV}\right) \qquad (2-19)$$

$$\frac{d^2U}{dV^2} = \frac{d}{dV} \left(\left(\frac{dU}{dR}\right) \left(\frac{dR}{dV} \right) \right)$$

$$= \frac{dU}{dR} \cdot \frac{d^2R}{dV^2} + \left(\frac{d^2U}{dR^2} \right) \left(\frac{dR}{dV} \right)^2 \qquad (2-20)$$

At the equilibrium seperation $R=R_o$ and $\left(\frac{dU}{dR}\right) = 0$ so that

$$B = \frac{1}{18 R_o} U(R \quad) \quad R = R_o \qquad (2-21)$$

$$\text{using} \quad \left(\frac{dR}{dV} \right)^2 = \frac{1}{36N^2R^4}$$

$$\left(\frac{dB}{dp} \right)_T = 1 - \left(\frac{+R_o^3}{27V} \right) U \left(R_o \right)$$

$$= 1 - \frac{18R_o . R^3_o}{27 . 2 . R^3_o} . \frac{U (R_o)}{U (R_o)} \qquad (2-22)$$

where $_T = 1/B$, is the compressibility and is defined as the reciprocal of the bulk modulus. Thus equation (2-22) may be written as:

$$\left(\frac{dB}{dp} \right)_T = 1 - \frac{R_o^3 \left(U \left(R_o \right) \right)}{3R_o^3 \left(U \left(R_o \right) \right)} \qquad (2\text{-}23)$$

2.3 The energy from the Born-Haber cycle:

The theoretical value of the lattice energy can be compared with the experimental value determined by a Born-Haber cycle analysis. In this method, one considers all the steps involved in transforming one mole of Ti, Si, Ge and Sn respectively and one mole of molecular oxygen gas into one mole of rutile. The energy associated with each step of the cycle can be determined from thermochemical data. The formula for the energy is:

$$U = 4H - L - D + 2A - I_4 \qquad (2\text{-}24)$$

where H is the heat of formation of rutile, L is the heat of vaporization of Ti, Si, Ge and Sn respectively, D is the disociation energy of O gas, A is the affinity of the oxygen atom for two electrons and I is the sum of the first four ionization potential of the Si, Ti, Ge and Sn atom respectively.

CHAPTER 3

REPULSIVE INTERACTIONS

3.1. Origin of Repulsive interaction:

A qualitative picture of the origin of the repulsive force may be given as follows:

When M^+ and X^- ions approach each other closely enough so that the orbitals of the electron in the ions begin to overlap each other, then the electron begins to repel each other by virtue of the repulsive electrostatic Coulomb force. Of course, the closer together the ions are, the greater the repulsive force, which is in qualitative agreement with experimental observation. Without paying attention to the physical origin of the forces between the atoms, let us assume that the potential energy of atom M due to the presence of atom X is given by an expression of the type:

$$U(r) = -\frac{\alpha}{r^n} + \frac{\beta}{r^m} \qquad (3-1)$$

where r is the distance between the nuclei of the two atoms; α, β, m and n are constants characteristic for the MX molecule. The zero of energy is chosen such that for infinite seperation, U=0. The first term, which is negative, corresponds to the energy associated with the force of attraction, the second(positive) term corresponds to the forces of repulsion. In fact, the force between that two atoms as a function of r is given by

$$F(r) = -\frac{dU}{dr} = -\frac{n\alpha}{r^{n+1}} + \frac{m\beta}{r^{m+1}} \qquad (3-2)$$

The energy and the force between two atoms M^+ and X^- which form a chemical compound are represented in Fig. 3-1(a), Fig. 3-1(b).

The stable configuration for the system corresponds to the minimum U(r) curve, which occurs for a particular seperation, $r=r_0$ The corresponding energy $U(r_0)$ is negative; thus the positive quantity $D= -U(r_0)$ is the dissociation energy of the molecule i.e. the energy required to seperate the two atoms.

Dissociation may occur, for example, at high temperatures or as a result of other process in which the mloecule can absorb sufficient energy. The dissociation energies are of the order of one or a few electorn volts.

Assuming that the energy curve exhibits a minimum, one may express the equilibrium distance r_0 and the corresponding binding energy $U(r_0)$ in terms of the constants α, β, m, and n by making use of the condition

$$\left(\frac{dU}{dr}\right)_{r=r_0} = 0 \quad \text{i.e.} \quad r_0^{m-n} = \left(\frac{m}{n}\right)\left(\frac{\beta}{\alpha}\right) \qquad (3-3)$$

According to (3-2) this condition is equivalent to the requirement that the attractive and repulsive forces balance i.e. F(r) = 0. substituting from (3-3) into (3-1) one obtains for the energy in the equilibrium state

$$U(r\ ) = -\frac{\alpha}{r_o^n} + \frac{\beta}{r_o^m} = -\left(\frac{\alpha}{r_o^n}\right)\left(1-\frac{n}{m}\right) \qquad (3\text{-}4)$$

It is noted that although attractive and repulsive forces are equal in equilibrium the attractive and requlsive energies are not equal since $n \neq m$. In fact if $m \gg n$, to total binding energy is essentially determined by the energy of attrction $-\frac{\alpha}{r_o^n}$

As one may expect already by looking at fig. 2-3(a), a minimum in the energy curve is possible only if $m > n$; thus the formation of a chemical bond requires that repulsive forces be of short range than the attractive ones. This may be shown by employing the condition that $\left(\frac{d^2U}{dr^2}\right)_{r=r_o} =0$ if must have a minimum at r_o . In fact, this condition leads to

$$-n(n+1)\frac{\alpha}{r_o^{n+2}} + \frac{m(m+1)}{r_o^{m+2}} > 0 \qquad (3\text{-}5)$$

which upon substitution of r_o from (3-3) immediately gives

$$m > n \qquad (3\text{-}6)$$

3.2 Different empirical forms:

i) Born-Lande potential (1918):

Many years ago Born and Lande[1] used an inverse power repulsive term in the potential function for alkali halide crystals. For gaseous ionic molecule Born-Lande proposed a potetial function in which the repulsive energy is expressed as:

$$\phi(r) = br^{-n} \tag{3-7}$$

where b and n are constants. This repulsive energy was much used in the potential energy during the twenties for investigating ionic crystals. Krebs[54] applied equation (3-7) to LiH and NaH and later paper[55] discussed the nature of alkali hydrides in the gaseous state. Rice[56] has determined the value of n from the lattice energy data and has used it to calculate the binding energy of gaseous alkali hydrides. The above equation has also been employed by Mulliken[57] in discussing the nature of the binding in LiH.

Investigation of interionic forces that have been carried out on the basis of quantum mechanical calculations of forces between ions showed that an inverse power repulsive term was not satisfactory. The calculated values of α_e(rotational constant and vibrational constants $\omega_e x_e$ are too high and the ionic binding energy D_i are too low. Thus it is found that BL potential is not satisfactory for alkali hydrides. However, it is interesting that for a particular constant (α_e, $\omega_e x_e$, or D_i) the percentage error is in the same direction, for all the molecules.

ii) Born-Mayer potential (1932):

In most applications of the Born model since 1930, the repulsive energy of the closed shell ions has been assumed to vary exponentially with their distances, in keeping with quantum mechanical results (Heitler and London[50] , 1927). The repulsive energy, as a function of the nearest-neighbour distance r, is expressed by Born and Mayer[2] (1932) in the form:

$$\phi(r) = a\, e^{-r/\rho} \tag{3-8}$$

where a and ρ are the repulsive parameter. The BL model is the most sucessful of the previous models. However, in other respects a representation of the repulsive term as good an exponential function (Born and Mayer). One argument that has been frequently advanced in support of the exponential function is that such a term is predicted by quantum mechanical calculations. Theoretical treatment of the repulsive forces between closed shell anion and point cations have tended to support the assignment of an exponential term. However, several of the theoretical results are in serious disagreement with the experimental data. Thus the available evidence suggests that present quantum mechanical treatments can not be applied to the representation of the binding energy in diatomic ionic crystals. Finally, as Dobbs and Jones[58] remark ''The exponential form for the repulsive potential makes calculation of the lattice propertes rather complicated and in any case is perhaps, not valid in the region near the minimum of the total potential which is of course the essential part in considering the properties of the lattices.''

iii) Wasastjerna potential (1935):

Wasastjerna[33,34] , in 1935 investigated an extended form of the repulsive potential for Na, Rb and Cs halide crystal. This is as follows:

$$\phi(r) = c\, r^7 e^{-\beta r} \tag{3-9}$$

where c and β are constants.
With the repulsive potential the Wasastjerna potential gives rise to nagative α_e (rotational constants). The vibrational constants $\omega_e x_e$ very high and the ionic binding energy D_i are excellent agreement with the observed ones. It is the remarkable phenomenon that it is able to reproduce one of the constant (D_i) very successful, but fails completely for the other two.

iv) Hellmann potential (1936):

Some 25 years ago, Hellmann[31,32] introduced the following repulsive potential in the potential energy to represent the interaction between the valence electron and the core in an alkali atom:

$$\phi(r) = -\frac{T}{r} \cdot C^{-\lambda r} \tag{3-10}$$

where T and λ are constants. Since then it has been used for the electron-core interaction by a number of workers[59-63]. However, as for as we have been able to find, this potential has never been used before as the interaction potential. It has been found that such a potential yields satisfactory results for rapresenting the shape of interatomic potential energy curves of alkali hydrides at least in the neighbourhood of the equilibrium internuclear distance.

v) HM potential:

M.L.Huggins and J.E.Mayer[64] in 1937 proposed a form of repulsive potential which is as follows:

$$W = M\beta_{++} b_{+} b_{-} e^{-r/} + \tfrac{1}{2}M \left(\beta_{++} b_{+}^{2} + \beta_{-} b_{-}^{2} + b\right) e^{-r/\rho} \qquad (3\text{-}11)$$

where b_+ and b_- are the charactristic parameters and the parameter ρ can be determined by a simultaneous fit for the salts of the family. It should be simultanuously emphasized that the fit of the repulsive parameters to crystal data is effectively used in the Born model to correct, in an appropriate way, the approximations made in the assumed expression of the lattice energy. The mean deviation of the values of n in the individual salts yielded by equation $n = \left(\frac{\alpha}{T}\right)-1$ from their mean value amounts to 6% as for the original Born-Mayer calculation, but the root-mean square deviation is as large and 10% as large discrepancies between the average and the individual value of n are apparent in a few salts. This implies that the Huggins-Mayer form of the Born repulsive energy does not provide a good fit of the compressibility for all the salts.

vi) Verwey potential (1946):

Verwey[65] in 1946 proposed a harder core potential function in which the repulsive every is expressed as:

$$\phi(r) = \mu r^{-12} \qquad (3-12)$$

where μ is the repulsive parameter. The Verwey potential have been used by workers (Guccione, Tosi and Asdente[66] 1959, Tharmalinghm[67] in 1963,1964, Boswarva and Lidiard[68] in 1967) in the calculations of activation energies and defect energies.

vii) Dick-Overhauser potential (1958):

Regardless of the attractive force between atoms it known that the atoms remain a finite distance apart at equilibrium. Thus a repulsive force must set in suddenly at short distances and balance the attractive force at the equilibrium distance between atoms. This repulsive force arises in part from the application of the Pauling exclusion principle, since the exclusion principle opposes the overlapping of the saturation electron clouds of the different atoms.

The simpliest mathematical form for a potential which yields a sudden repulsion at short distances is expressed within the Born-Mayer model[2] as $\phi = a\, e^{-r/\rho}$. The form of the potential is not obtained from first principles but, neverthless, represents the repulsive interaction satisfactorily between two ions, as for example, between two helium atoms or two neon atoms. However, as a general model the potential is quite unsuitable for the whole alkali halide series.

The electronic shells in the ions of alkali halides are closed shells and thus can be thought of as being similar to helium atoms except for the increased electronic and nuclear charges. It can reasonably expect that the results obtained from a study of the interaction of two atoms (helium) can be applied to the more general case of alkali halides. By evaluating the helium-helium interaction integrals, Dick and Overhauser[69] have shown that the total repulsion in this system can be represented by:

$$\phi = e \cdot Q_{ex} / 2r \qquad (3\text{-}13)$$

where Q_{ex} is the exchange charge. The nature of the exchange charge can be inferred from a considerable method of Lowdin's technique of symmetrical orthogonalization[70] , which takes into account the lack of orthogonality of the ionic electronic wave function due to overlap. When the value of $\Theta_{ex} = 4 e S_{MX}^2$ as determined by Hefemeister and Zahrt[71] is substituted in (3-13) becomes

$$\phi_{rep} = 2 . S_{MX}^2 e^2 / r \tag{3-14}$$

It may be noticed that the overlap integral S_{MX} in equation (3-14) is a complex function of r. Rather than being a single exponential it is the sum of number of exponentials, each with complex multiplicative terms. The Born-Mayer form for ϕ_{rep} is thus an oversimplification of the actual results.

viii) Varshni-Shukla potential (1961)

Varshni and Shukla[72] in 1961 proposed a more complicated form of potential for the repulsion between closed shell ions,

$$\phi_{rep} = \lambda_1 e^{-k_1 r^2} \tag{3-15}$$

Where λ_1 and k_1 are the repulsive parameters. Recently it has been found that the potential is reasonably satisfactory for the alkali halides. The rotational constants α_e for LiH and NaH negative, which is contrary to observation. Except for LiH, the vibrational constants $\omega_e x_e$ are 20% lower than the observed ones. The ionic binding energy D_i is satisfactory. But the potential is very much unsatisfactory in reproducing other molecular constants. For the above model, one has:

$$\lim_{r \to 0} U(r) = - \infty \tag{3-16}$$

ix) Benson-Dempsey potential (1962):

Jai Shanker et.al.[30] in 1981 used Benson-Dempsey[73] repulsive potential for analysis of interionic potential in alkaline earth fluoride crystals. The repulsive energy by taking into account the interaction between nearest and next nearest neighbour cation-cation, cation-anion and anion-anion can be written as follows:

$$\phi(r) = 8\beta_{+-} b e^{(r_+ + r_- - r)/\rho_{+-}} + 6\beta_{--} b\, e^{(2r_- - k_1 r)/\rho_{--}} + 6\beta_{++} b\, e^{(2r_+ - k_2 r)/\rho_{++}} + 12\beta_{--} b\, e^{(2r_- - K_2 r)/\rho_{--}} \qquad (3\text{-}17)$$

where β_{ij} are the co-efficients introduced by Pauling[74] is order to provide appropriate weightage for the various pair interactions. b and ρ_{ij} are the strength and hardness parameters. r_+ and r_- are the radii of cation and anion respectively; $k_1 = 1.1547$ and $k_2 = 1.6330$. Values of ρ_{ij} are derived using the correlation between repulsive energy and overlap integrals for the pair of neighbouring ions[74]

$$b_{ij}\, e^{-r_{ij}/\rho_{ij}} = 2\gamma e^2 S_{ij}^2 / r_{ij} \qquad (3\text{-}18)$$

where γ is a dimensionless proportionally constants introduced by Dick and Overhauser[69]. S_{ij} for various ion pairs in CaF_2 and BaF_2 crystals have been reported by Ra[75] . Values of ρ_{ij} based on these overlap integrals. The repulsive strength parameter b can be calculated from the crystal equilibrium condition. The cohesive energy obtained by Benson and Dempsey[73] are in slightly better agreement with experiment.

x) HF potential (1965):

The Hefemeister and Flygar[76] form of SR overlap repulsive energy extended to the next nearest neighbour ions with b and β_{ab} as the hardness and range parameters can be written as:

$$\phi(r) = \sum_{ab} \beta_{ab}\, b\, e^{r_a + r_b - r_{ab}/\rho_{ab}} \tag{3-19}$$

where a, b = 1, 2, ... and β_{ab} are the Pauling coefficients defined as:

$$\beta_{ab} = 1 + \frac{Z_l}{n_l} + \frac{Z_m}{n_m} \tag{3-20}$$

where Z_l and Z_m are the valencies and n_l and n_m the number of outermost electrons of the lth and mth ions. r_l and r_m are the ionic radii.

R.K. Singh and P. Khare[77] analaysed the anharmonic properties of silver thallium and copper halides by means of this interionic potential model incorporating the effects of the long-range coulomb and three body interactions and the short-range vdW attractive and overlap repulsion. The results by using HF potential agree fairly well with the avaiable experimental data and show a consistant trend through out.

xi) Modified Varshni-Shukla potential:

Patel, Gohel and Trivedi et.al.[5,78] adopted a slightly different potential function for the repulsion to that proposed by Varshni and Shukla[72]. Specifically, this potential function can be expressed as:

$$\phi(r) = {}_{2}e^{-k_2 r^{3/2}} \qquad (3-22)$$

where λ_2 and k_2 are the repulsive parameters. The rotational constants α_e are too high. The average percentage error of vibrational constant $\omega_e x_e$ is the lowest amongst the potential. The binding D_i are about 10% lower than the observed ones. For $\omega_e x_e$, (3-22) improves upon (3-10) but for average percentage error by (3-22) is nearly twice of that by (3-10).For D_i also , the results by (3-22) are uniformly less satisfactory than those by (3-10).

xii) HZ form of overlap repulsion potential:

R.K. singh and S.P. sanyal[79] used an overlap repulsion `potential for analysing the cohesive and thermodynamic properties of alkaline earth oxides by extending HF and HZ potentials to include the three-body interaction effects. The extended HZ [71] potential can be written as:

$$\phi(r) = Nb \sum_{ij} \frac{\beta_{ij}}{r_{ij}} e^{(r_i + r_j - r_{ij})/\rho_{ij}} \qquad (3-23)$$

where i and j denotes respectively either ion 1 or 2; β_{ij} are the Pauling co-efficients defined as:

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \qquad (3-24)$$

with Z_i (Z_j) and n_i (n_j) as the ionic charge parameters (± 2) and the numbers of electrons (= 8) in the outermost shells of cations and anions; r_i and r_j are the ionic radii whose values have been taken from Pauling[74]. The cohesive energies calculated from the present extended HZ form of potential are in better agreement with experimental data than those obtained by previous investigators. It is also seen that the results obtained with HZ potential are much better than those of the HF potential. The extended HZ potential has yielded results much closer to the experimental results on cohesive energy, its overall superiority has been obtained by performing calculations of various thermophysical properties of AEO crystals.

xiii) GT potential (1968):

The appropriateness of the Born-theory of ionic crystals is being successfully for alkali hydride crystals for which a little work is available in literature. A new form of overlap repulsion energy term[80] for alkali hydride earlier suggested by Gohel and Trivedi[45] for alkali halides of the form.

$$\phi(r) = P/r\ e^{-k\,r^2} \qquad (3-24a)$$

where P and K are the repulsive parameters and r is the interionic distance. This form (3-24a) has been suggested to study the lattice properties of hydrides.

The crystal energy may be expressed as the sum of coulombian attraction energy, the overlap repulsive energy, the point energy and the van der Waals interaction energy terms. The compressibility predicted by[80] and is superior to those predicted by Das and Sexena[35] . The co-efficient of thermal expansion is good agreement with the experimental value.

xiv) Prakash-Behari logarithmic potential (1969):

Prakash and Behari[81] suggested a logarithmic form repulsive energy in ionic crystals that has subsequently been adopted by Mishra et. al.[72] (1971) and by Sharma and Jain[83] in 1973, to study the properties of these crystals. The new potential is given by

$$\phi(r) = a \log (b + br^{-9}) \qquad (3\text{-}25)$$

where a and b are the repulsive parameters. It has been found that depends sensitively on the form of the potential for the repulsive energy used within the frame work of the Born model. It should be remarked that the logarithmic potentials yield almost identical values of the cohesive energies and that these are consistently higher in magnitude than those based on experimental thermodynamic data. In contrast, the values of δ derived from these two forms of potential Verway and log.differ significantly each other.

xv) Redington potential (1970):

Redington[14] in 1970 proposed a form of repulsive potential

which can be represented by:

$$\phi(r) = a_1 e^{-\beta r} + a_2 e^{-\beta r/2} + a_3 e^{-\beta r/3} \qquad (3-26)$$

where a_1, a_2 and a_3 are some constants and β is the repulsive parametrs.

xvi) Katiyar potential (1970):

For the analysis of interionic potential in rutile structure MX_2 crystals corresponding to MRIM, Katiyar[84] presented a SR repulsive energy given by

$$\phi(r) = 4\,\psi_1(R_1) + 8\,\psi_2(R_2) + 16\,\psi_3(R_3) + 2\,\psi_4(R_4) \qquad (3-27)$$

where R_1, R_2, R_3 and R_4 are the four different cation-anion, and anion-anion distances in rutile structure defined by Striefler and Barsch.[36]

$$\text{where}\quad \psi_1(R_1) = B_{+-}\, b\, e^{(r_+ + r_- - K_1 R)/\rho_{+-}} \qquad (3-28)$$

$$\psi_2(R_2) = B_{+-}\, b\, e^{(r_+ + r_- - k_2 R)/\rho_{+-}} \qquad (3-29)$$

$$\psi_3(R_3) = B_{--}\, e^{(2r_- - k_3 R)/\rho_{--}} \qquad (3-30)$$

$$\psi_4(R_4) = B_{--}\, e^{(2r_- - k_4 R)/\rho_{--}} \qquad (3-31)$$

where b and ρ are the strength and range parmaters, respectively, k (i = 1 - - - - 4) are the dimensionless factors defined by Striefler and Barsch[36], (1973), B are the Pauling co-effecients (Singh and Tiwary[85], 1980) introduced to provide appropriate weighting for different ion-pair interactions and r_+ and r_- are the crystalline radii of cations and anions.

xvii) RMS potential (1974):

The repulsive energy contribution to the lattice energy per ion pair in an NaCl-type crystal has been proposed by [86] as follow

$$\phi(r) = 6 \cdot B_u\, e^{-\alpha r} + 6\, B_1\, e^{-\sqrt{2}\alpha r} + 8\, B_u\, e^{-\sqrt{3}\alpha r} + 3\, B_1 \cdot e\; e^{-2\alpha r} + 24\, B_u\, e^{-\sqrt{5}\alpha r} \qquad (3\text{-}32)$$

where interactions upto fifth neighbours are included. The parameters α, B_u, B_1 are determined crystal by crystal data at atmospheric pressure and at temperature in the range 300 - 700 K via the Hildebrand equation of state.

One can make a comparison of the potential with the Fumi and Tosi [87] potential by performing calculations for NaCl, KCl & KBr. The comparison shows that the FT potential and RMS potential as reported gives quite comparable values for the total repulsive energy contribution to the lattice energies per ion pair a function of the nearest neighbour distance around the equilibrium value in standard thermodymanical conditions, but that the RMS potential gives much smaller values than FT potential for the repulsive energy contribution due to the nearest and next nearest neighbours.

xviii) Thakur potential (1976).

For many of the previous model it is found that

$$\lim_{r \to 0} U(r) = \infty \qquad (3-33)$$

and thus the potential energy curves will approach infinity in the negative energy region. The exponential repulsion terms suffer from the fundamental physical draw back that they gave a constant finite value at $r \to 0$. The forms of the pair potential for an LiF crystal as predicted by the models BL [1], BM [2], VS[72], & PGT[5] are shown in figure 3 - 1 , where it is seen that, after the usual minimum at equilibrium ionic seperation r_0 , the curves have a minimum in the region $r < r_0$ and tend to infinity as $r \to 0$. The height of the potential barrier for the BL model is about 10^5 kj/mol; very much greater than for the other model.

The potential energy curves in fig. 3-1 as predicted by these models are not satisfactory. Since there must be a finite probability for penetration of ions in each direction through the potenial barrier under these condition a crystal would not remain stable and could

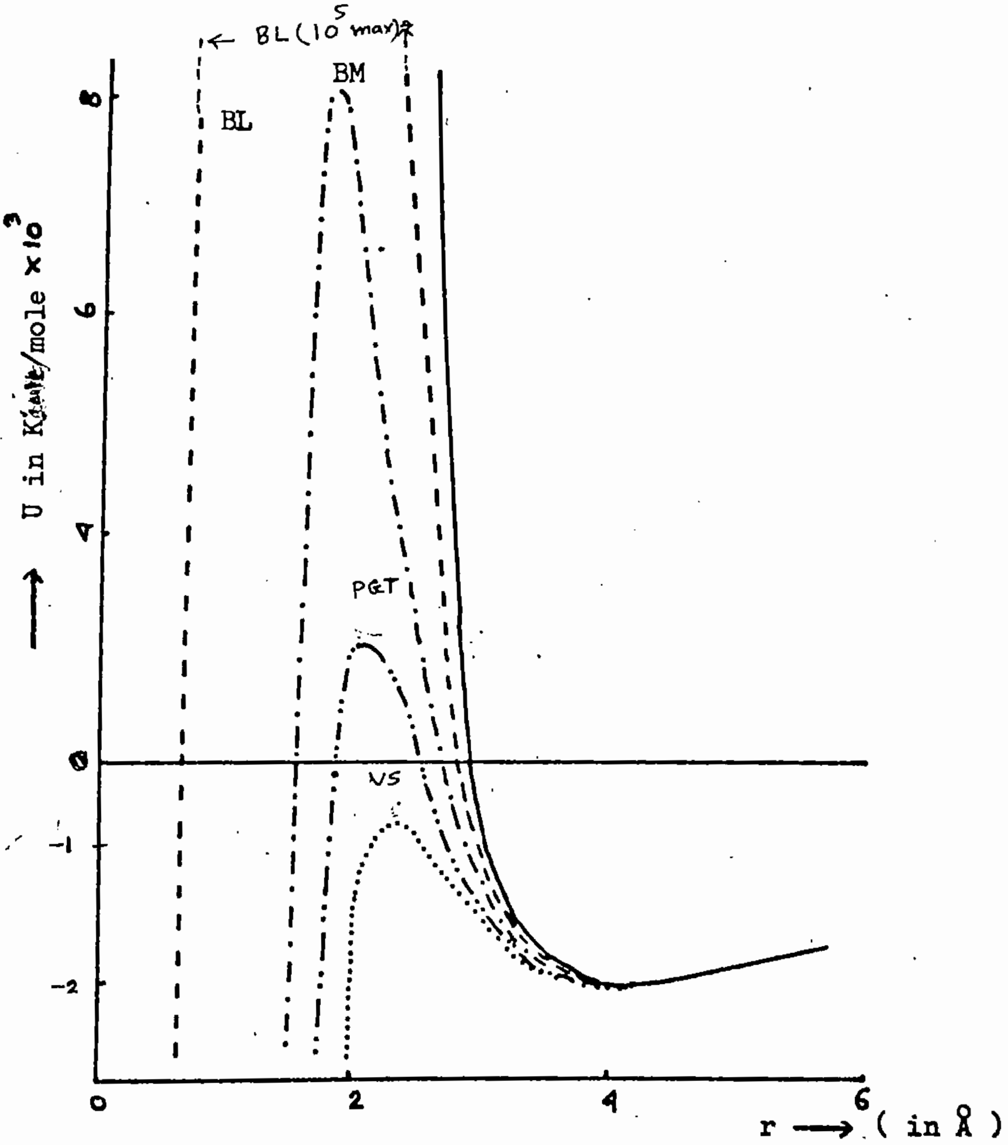


Fig. : 3-1 : Potential energy curves.

either collapse or contain heavier muclei formed by fusion following such tunneling. There is no evidence to show that diatomic ionic crystals have these characteristics.

The force $F(r) = -\frac{dU(r)}{dr}$ between an ion pair, as given by the models BL, BM, VS & PGT, is plotted as a function of the ionic seperation r in fig. 3 - 2 . Again the curves are not satisfactory since they all give F(r) zero for two values of r indicating a stable crystal for two values of ionic radius, together with the possibilities of crystals collapse and the formation of the heavier nuclei by the application of an external force equal to he height of the force curve.

For predicting the form of the potential energy curve then, from the above discussion the BL model[1] is the most successful to the previous models. However in other respects an inverse power function is not as good a representation of the repulsive term as exponential function. One argument that has been frequently advanced in support of the exponential function is that such a term is predicted by quantum mechanical calculations. Theoretical treatments of the repulsive force between closed shell anions and point cations and between inert-gas atoms have tended to support the assig-

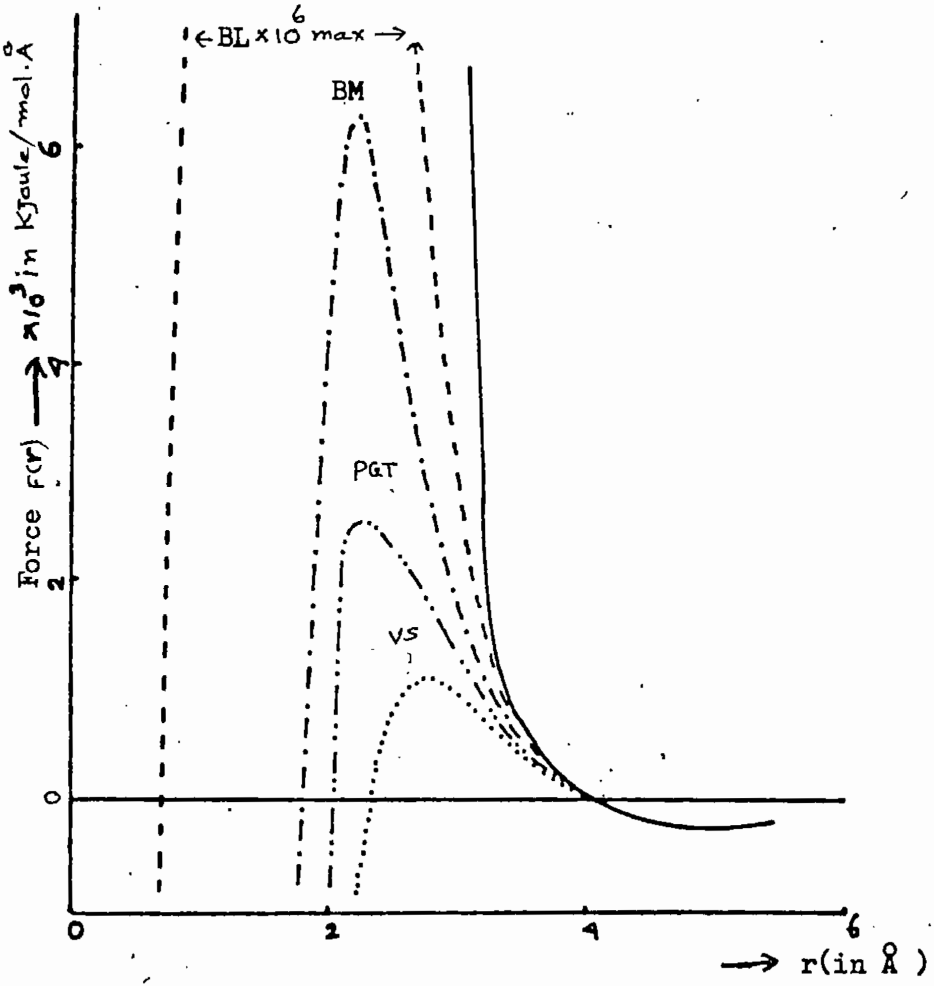


Fig. - 3-2 : Force curves(interionic force) nment of an exponential form. However, several of the theoretical result are in serious disaggrement with the experimental data. Thus the available evidence suggest that present quantum mechanical treatments cannot be applied to the representation of the binding in diatomic ionic crystals. Dobbs and Jones[58] remarks "The exponential form for the repulsive potential makes calculations of the lattice properties rather complicated and, if any case, is perhaps, not valid in the region near the minimum of the total potential which is of course the essential part in considering the properties of the lattices."

Until a complete mechanical treatment of ions in close contact is available, the overall effect of the short-range forces can only be represented by an empirical term in any model of the potential energy. However-,existing models above are not entirely satisfactory and it would seen worthwhile to consider an alternative form for the repulsive potential term. It is accepted that this form will not only be adequate representation within the region $r > r_x$, where, r_x is the interionic distance at which the electronic shells come into contat. In accordance with Pauling principle the short-range repulsion should become infinty when the closed shell electron clouds of the anion and cation overlap and taking account of this, the following logarithmic form[88] for the repulsive potential is proposed:

$$\phi(r) = P \log (1 + p' r^{-n}) \tag{3-34}$$

where P and p′ and n are the constants. With inclusion of the terms for the other interactions, the final form for the potential energy of the ion pair is then

$$U(r) = - \frac{Ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} - \frac{Kle^2}{r^{10}} + P \log (1 + p\ r\ \ ) + \tag{3-35}$$

The last two terms of this equation may be combined to give

$$P \log (1 + p\ r\ \ ) = P \log (a + p\ r\ \ ) \tag{3-36}$$

where $\mathcal{E}$ = P log a now represents the zero point energy and P = ap′. The model proposed by Thakur[88] is investigated for a parameter value of n = 6. The form of the present potetial function is satisfactory since unlike the previous curves it has a single turning point at $(U(r_0),r_0)$ and tends to infinity in the +ve energy domain outside region $o<r<r_x$.

The previous proposed models for the potential energy function in an ionic crystal are not entirely satisfactory. In order to overcome these difficulties this new repulsive interaction has been proposed in which the interionic potential energy tends to infinity in the positive energy domain. It has been found that the new model gives a better representation of the experimental data for the cohesive energy, the Gruneisen and Anderson - Gruneisen parametes and reststrahlen frequency than previous models, and is comparable in its predictions of the atomization energy.

The form for the potential proposed is an improvement on previous models and although far from perfect, it may help in obtaining a better understanding of the nature of the ionic bond.

xix) SKM potential (1977):

The main feature of the existing potential models which have been suggested so far is the direct functional depedence of potential energy on the interionic distance at equilibrium.

Actually the force of repulsion depends directly on the depth of overlaping of wave functions of the outer most orbits and thus it will be appropriate to assign, such a form of the repulsive energy term which is function of interorbital distance.

Introducing the concept of interorbital distance instead of interionic distance for ionic crystals a new form of overlap repulsion energy was proposed by M.N.Sharma et.al[39](1977). The form of overlap repulsion[39] is as follws:

$$\phi(r) = f\ (\delta_1) \qquad (3\text{-}37)$$

where f(δ_1) is a function of interorbital distance. Assuming ϕ (R) to be function of δ_1 , the potential energy per unit in an ionic crystal may be expressed as

$$U(r) = -\frac{e^2}{r} + \phi(R) - \frac{C}{r^6} - \frac{D}{r^8} \qquad (3\text{-}38)$$

where the notations have their usual meaning. To determine the form of the repulsive potential the values of δ_1 were determined by the following method.

For NaCl-type crystal each metal ion is surrounded by six nearest neighbour halogen ions, four of which can be taken in the same plane with the central metal ion. The distance between the centres of the two opposite halogen ions can be determined as $2r_-\sqrt{2}$, half of which will be equal to the distance between centres of metal and halogen ion. Thus

$$= (\ r_-\sqrt{2} - (r_+ - r_-)\ )$$

$$= (\ 0.414\ r_- - r_+\ ) \qquad (3\text{-}39)$$

similarly for CsCl type crystals

$$= (0.732 r_- - r_+) \qquad (3\text{-}40)$$

Thus one can obtain as : $\phi(r) = A\,\delta_1^n$ (3-41)

where A and n are potential parameters.

This model is more suitable for predicting the behavour of alkali halide crystals regarding infrared absorption frequency as compared to previous values by other workers. Though its performance is poorer for flurides among other crystals, the model shows a marked improvement in the case of fluorides as compared to the results obtained with other model. Thus the overall performances of the properties of the crystals shows a marked improvement to the previous models. The uniform behaviour of the crystal properties may be observed which was one the short-comings of the previous models.

xx) Mohammed potential (1979):

S. Noor Mohammad[42] proposed a general form for repulsive potential of the given below:

$$\phi(r) = S\, e^{-\eta r^m/r^n} \tag{3-42}$$

where S, η, m and n are the parameters of the potential. With this form for $\phi(r)$ the total potential energy can be writen:

$$U(r) = -\frac{Z_M Z_X e^2}{r} + S\, e^{-\eta r^m/r^n} - 0.5e^{2}\frac{(\alpha_M + \alpha_X)}{r^4} - \frac{C}{r^6} - \frac{2e^2{}_M\alpha_X}{r^2} \tag{3-43}$$

In equation (3-45) α_M and α_X are the polarizabilities and Z_M and Z_X are the atomic weights of the M^+ and X^- and C is the van der Waals constants, given by

$$C = 1.5\alpha_M \alpha_X I_M E_X/(I_M + E_X) \tag{3-44}$$

I_M is the second ionization potential of the ions and E is the electron affinity of the negative ion.

It is possible to derive this potential from a series of empirical consideration. In order to derive the improved model we assume that the total potential energy of a system is $E = E_1 + E_2 + E_3$, where E_1 is the combination of the exchange and Coulomb energies and $E_1 + E_2$ arises from the polarization of charges of the ions of the system. Other contributions to E are assumed negligble. The electronic energy E depends largely on the charge density in the bond region. To determine it we then be used the charge density model of Anderson and Parr can be used. We then write

$$\nabla^2 E_1 = F_1(r) \approx 4\pi Z_{\alpha'} \rho_{\beta'}(\alpha') = 4\pi Z_{\beta'} \qquad (3\text{-}45)$$

where $Z_{\alpha'}$ is the atomic number of nucleus α' and $\rho_{\beta'}(\alpha')$ is the first-order electron density at nucleus due to the part of the total electron density which perfectly follows nucleus during vibration. Each first order density function F_1 (r) in equation (3-45) determines a potential $E_1(r)$ and conversely. The simpliest possible assumption about $\rho_{\beta'}(\alpha')$ may be that it is exponentially decaying and with this assumption we take F_1 (r) as

$$F_1(r) = S\, e^{-\eta r^m/r^{n+2}} \left(n^2 m^2 r^{2m} - nm(m - 2n + 1) r^m + n(n-1) \right) \qquad (3\text{-}46)$$

in which η, S, m and n are the parameters of the function $F_1(r)$; with this function we get from equation (3-45)

$$E_1(r) = -e^2/r + S\, e^{-\eta r^m/r^n} \qquad (3\text{-}47)$$

In order to determine E_2 and E_3 (considering only term which are zeroth order in overlap) we write the interaction potential V as a multiple expansion. Using the relation due to Buckingham, one can write

$$V = t\, q_1 q_2 + t_\alpha\, (q_1 \mu_2 - q_2 \mu_{1\alpha}) + t\, \{ 1/3 q_1 \Theta_2 + 1/3 q_1 \Theta_1 - \quad) + \ldots\ldots\ldots\ldots \qquad (3\text{-}48)$$

Index 1 refers to M^+ and index 2 to X^-. The quantities q_i, μ_i, Θ_i are respectively, the monopole, dipole and quadrupole operators associated with specis i(i = 1, 2). With this V, E_2 and E_3 can be approximated as

$$E_2(r) + E_3(r) \approx -0.5\ e^2(\alpha_M\ \alpha_X)/r^4\ \frac{C}{r^6} - 2\ e^2 \alpha_M \alpha_X / r^7 \qquad (3\text{-}49)$$

Sum of E_1, E_2 and E_3 given the potential U(r) as in equation (3-43).

Comparison to other potentials:

The average percentage errors for quantities for all the system of alkali halide series it can be stated that the new potential with variable m predicts consistently better results than the other. It has been observed that with m = 1.4 and n = 1.75 the proposed can also given satisfactory results. The calculated values of the spectroscopic constants are quite poor. However these values using thus new potential with vairable m are better than using Rittner's potential[3]. Thus the proposed potential with variable m is more flexable and much better than the Rittner potential[3].

Defect of the potential:

The main defect of the potential is that it is a semiemperical one and uses either the free ion polarizabilities (α_M, α_X) or the crystal polarizabilities as input. Since one can use in principle only the effective polarizabilities $(\alpha_M^{eff.}, \alpha_X^{eff.})$ viz., the polarizabilities of the ions as part of the alkali halide molecules, the use of any of these two should lead to inaccurate results. The crystal polarizabilities can not be used since they differ greatly from the effective polarizabilities. The free-ion polarizabilities can not be used because the polarizability of a positive ion M^+ is increased in the coulomb field of an anion, while the polarizability of a negative ion X^-, is decreased in the coulomb field of a cation.

xxi) Islam potential (1980):

The simple Born-Mayer potential compared to other form has been fairly successful in predicting some of the properties of the ionic compounds with NaCl structure. But for bivalent metal oxides, sulphides, selenides and tellurides having NaCl structure and other ionic compounds with different structures the results seem to be less satisfactory. Similar conclusions can also be made for other available potential, some of which are suitable for one of the crystals and not for other and vice-versa.

The available repulsive terms in their simple form thus do not describe the interaction energy properly at all distances and involving cation and anion which differ considerably in size from each other. Moreover, the lattice energy generally is larger for compounds containing atoms of higher valency than for compounds containing atoms of lower valency. It is stated that this in not fully understood by the difference in coulomb interactions and by the repulsion of simple exponential type. Thus a potential is needed which will not too be difficult to handle and at the same time it gives a simple dependence on the charge and the relative sizes of the ions and be able to account for the difference in structure type.

In view of the above considerations a modified short-range repulsive potential has been suggested by Islam[89] in 1980 which is as follows:

$$\phi(r) = I \quad e^{-S\ r^{\sigma}} \qquad (3\text{-}50)$$

Where $\sigma = Z + \frac{d}{2r_o}$; r and d are equilibrium ionic seperation and the difference of the ionic radii, Z is largest common factor of the valencies of the cation and anion. I and S are two parrmeters of the potential.

This specific form of the potential has been tested by calculating the crystals energy and the Anderson-Gruneisen parameters of the alkali halides, alkaline earth chalcogenides and titanium dioxide (rutile). The interaction potential includes the Coulmob, the two-body overlap confined to nearest neighbour and the van der Waals interactions which approximate the dipole-dipole and dipole-quadrupole attractions.

The lattice energy calculated using the Born-Mayer form showed significant deviation (average 7%), compared with either the present[89] (4.1%) or the Thakur's form[88] (4.7%).The overall prediction becomes much better with the present potential than obtained using Thakur's form.Thus the chief merit of the suggested potential lies in the fact that it leads to a good conection between the observed and the calculated results not only for simple NaCl type crystals but also for a wide varity of ionic crystals.

xxii) Harrison potential (1981):

Harrison[26] has presented a quantum mechanical treatment of the short -range repulsive energy can be written as:

$$\phi(r) = nh^2/2m\, \bar{\mu}^3 r\, e^{-k\bar{\mu} r} \qquad (3\text{-}51)$$

where r is interionic distance, n is adjustable parameter, h planck's constant divided 2π, m the electron mass, k a numerical factor taken as 5/3 by Harrison, equal for the kinetic energy term. $\bar{\mu}$ is an average of the quantities μ_1 and μ_2 for cations and anions respectively, such that μ is related to the valence p state energy ϵ_p as given below:

$$\epsilon_p = -\frac{h^2\mu^2}{2m} \qquad (3\text{-}52)$$

On the basis of (3-34) one can write the total overlap repulsion energy $\phi(r)$ extended up to second neighbour ions as follows:

$$\phi(r) = \frac{6nh^2}{2m} \left(\bar{\mu}^3 r \cdot e^{-k\bar{\mu} r} + \sqrt{2}\, \mu_1^3\, r \cdot e^{-k\sqrt{2}\mu_1 r} + \sqrt{2}\, \mu_2^3\, r \cdot e^{-k\sqrt{2}\mu_2 r} \right) \qquad (3\text{-}53)$$

where r is the nearest neighbour distance and r is the second neighbour distance in the NaCl structure solids. The Harrison repulsive potential is represented by a quantum mechanical analytical potential form derived from the tight binding theory. Accordind to J.Shanker and G.D. Jain[25], we have used the Born-Mayer potential for mixed crystals by taking the repulsive hardness parameter corresponding to overlap integrals. The results using Harrison's potential for mixed obtained in the study are in better aggrement with experimental data obtain the corresponding values obtained from the

Born-Mayer potential for mixed crystals[25].

xxiii) Narayan-Ramaseshan potential (1982):

In the compressible ion model[90,91] a radius is associated with an ion in the direction of each of its nearest and next nearest neighbour. The ions are then pictured to be in the form of a polyhedron, whose faces are perpendicular to the interionic bonds at distances from the ions centre equal to the corresponding radii. For each bond the sum of the radii of ions is taken to be equal to the bond length and so the whole crystal is made up of space filling polyhedra. The compression energy at the face i of an ions of polyhedral shape is assumed to be of the form[90,91]:

$$\phi(r) = B/2\pi \iint e^{-r'(S)/\sigma}\, ds \qquad (3\text{-}54)$$

where $r'(s)$ is the distance from the centre of the cell to an area element ds on the face and the integral is over the face area. B and σ are the repulsion parameters for the ions under consideration. The cell face can be approximated to a circle of equal area (Narayan and Ramaseshan) and one can then write the compression energy of the ith face as:

$$\phi(r)_i = B\sigma\big[(r_i + \sigma)\, e^{-r_i/\sigma} - (l_i + \sigma) e^{-l_i/\sigma} \qquad (3\text{-}55)$$

where r_i is the distance to the ith face from the ion centre and l_i is the distance to the circumstance of the corresponding circular cell face. The l_i 's depend on the interionic distance r as well as the crystal structure . The above theory of repulsion has been rather successful in explaining the structure of the alkali halides and is a natural choice for the others studies.

In calculations on the alkaline earth chalcogenides, the repulsive energy was computed using the simplified formula $l_i = \frac{r_i}{1 - 2/n + k(r_i/r_{av} - 1)}$. The actual procedure of the optimising the repulsion parameters B and ρ is explained elsewhere (Narayan and Ramaseshan[46,90], 1976, 1979)

The free energy per molecule of the crystal is given by

$$U_L = -\frac{Ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + \phi_{rep} + pv \qquad (3-56)$$

where r is the nearest neighbour distance, p the pressur and volume per molecule. The Madelung constants A is known for structure of interest. The van der Waals co-efficients C and D be calculated in terms of the polarizabilities of the ions and the effective numbers of participating electrons. However, it has been shown that the polarizabilities of the chalcogen ions can not be considered to be constants but must be taken to vary in the form.

(3-57)

The above theory of repulsion has been rather successful in explaining the structures of the alkali halides[45]. Detailed formula are given by Narayan & Ramaseshan for NaCl, CsCl and ZnS structures. However, the labour involved in deriving exact formula for the different l_i can become quite excessive when one deals with other lower symmetry structures and this would defeat the very purpose of the present approach which seeks to develop a simple semiemperical theory of repulsion. Instead an alternative simplified approach is presented here where l_i is computed in terms of only the co-ordination number and ionic radii.

If there are n faces symmetriclly disposed at equal distance from the ion centre, the solid angle subtended by each face at the centre is $\phi = \frac{4\pi}{n}$. If the n faces are at different distances r_i from the centre, a weighted average distance r_{av} may be defined as

$$r_{av} = 1/n \sum_i r_i \qquad \text{---} \qquad (3-58)$$

If $r_i < r_{av}$ the solid angle subtended by such a face will be greater than $\frac{4\pi}{n}$ while the reverse will be true when $r_i > r_{av}$. Motivated by this one can approximately write,

$$\phi_i = 4 \left(\frac{1}{n} + \frac{K}{2} \left(1 - \left(\frac{r_i}{r_{av}} \right) \right) \right) \qquad (3-59)$$

where we ϕ_i is written in a form which ensures that $_i \phi_i = 4\pi$.
K is a suitable constants which has to be determined.
It can be easily shown that equation (3-59) leads to the following relation for l_i

$$l_i = \frac{r_i}{1 - 2/n + K\,(r_i/r_{av} - 1)} \qquad (3\text{-}60)$$

The constants K=0.85 has been found by a least squares fit to the known exact values of the l_i's in the NaCl, CsCl, and ZnS structures.

The main advantage of the relation (3-60) is that only input required for calculation of l are the number of nearest neighbour and the corresponding radii.

Using the repulsive parameters of the chalcogen ions, one can determine the repulsion parameters for the other divalent cations. However, considering the low compressibility of the cations compared to anions, one can assume the cations to be hard spheres to a radius which can be fitted to reproduce the experimental interionic distance of the corresponding chalcogenides.

The compressible ion theory of repulsion has been applied to the alkaline earth chalcogenides using a simplified formulation of the polyhedral cell approach.The theory correctly shows that most of the crystals should occur in the NaCl structure. The repulsion parameters of the chalcogenide ions have been used to derive hard sphere radii for few divalent ions. Also the theory has been extended to the rutile and perovskite where the interionic distances and compressibilities are satisfactorily predicted. These results indicate that the theory, which is based on a purely ionic picture, is quite valid for divalent ions in crystals. However there is a mild discrepancy in the matter of relative stability of different crystals structure. The approach appears to over-estimate the stability of the NaCl structure and underestimate the binding energies of the competing ZnO and CsCl structures. The presence of the covalency might possibly explain the discrepancy.

xxiv) Satyanarayana potential (1984):

An empirical expression for the repulsion energy has been proposed for computing the lattice energies of alkaline earth chalcogenides and alkali halides in view of the short-comings of earlier forms[92] which is given by:

$$\phi(r) = Mb\,(e^{r/p} - 1)^{-1} \qquad (3\text{-}61)$$

where M is the number of nearest neighbour, and b and p are repulsion parameters to be determined under static equilibrium conditions from crystal data. The defensibility of the present form equation (3-61) is discussed in details below. Expanding equation (3-61) in a power series one obtains,

$$\begin{aligned}\phi(r) &= M\,b\,e^{-r/p}(1 + e^{-r/p} + e^{-2r/p} + \ldots\ldots)\\ &= M\,b\,e^{-r/p}\Big(\sum_{n=0} e^{-nr/p}\Big)\end{aligned} \qquad (3\text{-}62)$$

Generally p is of the order of 1/10 of r, and hence r/p will be of the order of 10. Therefore the sum of the infinite series is a rapidly converging one, and hence, to a good approximation, the series sum can be truncated at the second term. In this approximation the expression for the repulsion energy can be written as:

$$\phi(r) = M\ b\ e^{-r/p}(1+e^{-r/p}) = M\ b\ e^{-r/p} + M\ be^{-2r/p}$$

$$= \phi_{r_1}+\phi_{r_2} \qquad (3-63)$$

This results in a two term expression for the repulsion energy, the first term being simple BM form. For NaCl-type crystal structure the formula for repulsion energy is

$$\phi(r) = M\ b\ e^{-r/p} + 15\ A\ e^{-2r/p} \qquad (3-64)$$

and for CsCl - type crystal structure it is

$$\phi\ (r) = M\ b\ e^{-r/p} + 28\ \ A\ e^{-2r/p} \qquad (3-65)$$

where A's are the structure-independent constants accounting for the short-range three body interactions.

xxv) Yadav potential (1985):

Yadav[93] proposed a new repulsion term in the ionic interaction potential. The form of the potential is as follows:

$$\phi\ (r) = A\ r^{-n}e^{-r/\lambda} \qquad (3-66)$$

where A, n and λ are constants. He has utilized this to determine the cohesive energy of several alkali halide crystals. In going through this work some discrepancies are found in the evaluation of the potential parameters which leads the theoretical results meaningless.

The total potential energy of the alkali halide crystals is given by:

$$U(r) = \frac{e^2 Z_1 Z_2 \alpha}{r} + A\, r^{-n} e^{-r/\lambda} \tag{3-67}$$

There are three unknown parameters namely, A, n and which can not be obtained by solving then above equation. Varshni[94] and Varshni and Shukla[95] have used experimental vibrational energy of the crystals in computing the unknown parameters. Yadav[93] on the other hand, has introduced an arbitrary condition

$$\frac{d\,\phi(r)}{dv} = A\, r^{-3} \tag{3-68}$$

But
$$\frac{d\,\phi(r)}{dv} = \frac{r}{3v} \cdot \frac{d\phi\,(r)}{dr} \tag{3-69}$$

and the explicit form of above equation (3-66) with the help of (3-68) and (3-69)

$$\frac{d\,\phi\,(r)}{dr} = \frac{r}{3r} \left(- \frac{e^2 Z_1 Z_2 \alpha}{r^2} + \frac{A}{\lambda} r^{-(n+1)} e^{-r/\lambda} (n + \frac{r}{\lambda} \right) \tag{3-72}$$

Equation (3-66) and (3-58) are identical and a comparison of these equations shows that while the explicit form of $\frac{d\,\phi(r)}{dr}$ constants all the three parameters, A, n and λ, Yadav suppresses λ and n. He could have chosen $\frac{d\phi(r)}{dr} = A\ r^{-m}$, with m = 1, 2, 3, 4 or any other interger. The equation (3-66) thus constitutes a serious restriction on the form of potential function and is not warranted by any stability condition about the lattice. Moreover since the equation is not written at the equilibrium, it should be true for any value of r. On the other hand if the equation (3-67) were written for the equilibrium value, the right hand side of the equation should be zero. This point has been missed by Yadav[93] and in order to evaluate the model parameter he has used $\frac{d\phi(r)}{dr}\Big|_{r=r_o} = A\, r_o^{-3}$ and not zero. To prove, this is trivial but given here in order to clearify this point.

Write $\frac{d\phi(r)}{dr}\Big|_{r=r_o} = A\, r_o^{-3}$

Then $\frac{d\phi}{dr}\Big|_{r=r_o} = \frac{d\phi}{dv}\Big|_{r=r_o} \cdot \frac{dv}{dr}\Big|_{r=r_o} = A\, r_o^{-3} . 3Kr_o^{2}$ or

$$\frac{d\phi}{dr}\Big|_{r=r_o} = \frac{3AK}{r_o}$$

thus $d^2\phi/dr^2\Big|_{r=r_o} = -\frac{3KA}{r_o^2}$ and now equating $\phi''\Big|_{r=r_o} = \frac{9Kr_o}{\beta}$ from equation (3-69) for Yadav, we have the result of Yadav[93]. Thus shows the Yadav has used $\phi'(r)\Big|_{r=r_o} = 0$ and $\frac{3AK}{r_o}$ at the same time to determine the model parameters which makes his theoretical results invalid.

xxvi) Potential of Buckingham type:-

In our study we would also use a short-range potential of the familar Buckingham type

$$\phi(r) = Ae^{-r/p} - C/r^6 \qquad (3\text{-}73)$$

where the constant have their usual meanings. James and Catlow [159]while studing the interionic potential derived the various interactions utilizing Shell model.

A major problem in deriving such potentials for oxide crystals is the lack of experimental datas. This problem has been overcome by using the following assumptions:

i) The $O^{2-}-O^{2-}$ interaction is taken to be the same for all crystals and the potential derived by James and Catlow is used. At equilibrium oxygen-oxygen seperations this interaction is very small.

ii) Cation-cation interactions are assumped to be purely Coulombic. Since cations generally smaller than the oxygen ion and $O^{2-}-O^{2-}$ interaction already very small at equilibrium lattice spacings this assuption seems to be resonable.

iii) The cation-anion interaction is considered to be of the Born-Mayer form

$$\phi = A\, e^{-r/p} \tag{3-74}$$

i.e. the attractive r^{-6} term is ignored. The small contribution of such terms to the short-range potential at the lattice interatomic spacing will be incorporporated by small modifications of the Born-Mayer parameters.

XXVii) A new proposed form:

Many of the repulsive potentials proposed thus far suffer from some fundamental drawbacks. As r->o, the repulsive forms consisting of exponential term give finite values. As a result the potential energy predicted by previous models are not satisfatory and hence there must be a finite probability for ions in each direction through the potential barrier, under these conditions a crystal would not remain stable and could either collapse or contain heavier nuclei formed by fusion following such tunnelling. Evidence shows that the crystals donot have these characteristics.

In fig. 3-2 the force $f(r) = -\frac{dU(r)}{dr} = 0$ for two values of r, which indicates that the crystal is stable for two values of ionic radius. Thus U(r) and hence $\phi(r)$ is not satisfactory due to this possibilities in addition to collapse and to formation of heavier nuclei by the application of an external force equal to the height of the force curve. The electronic shells of the ions in question will have overlapped long before the interionic seperation has been reduced to (1-2) Å the ions $M^+(M^+)$, $X^-(X^-)$ can not exist in the region and an interionic potential as such cannot be defined in such a distance.

Taking this point in consideration, we are thus encouraged to propose~~d~~ the modified form of the existing potential due to Islam[89] as follows:

Ø(r) = G/(r**n) exp [-g (r**Sigma)]

where Sigma = z+d/zr, G and g are two parameters of the potential.

This form is in conformity with the Pauling principle according to which the short-range repulsion should become infinite when the closed-shell electron clouds of the anion and cation overlap.

The crystal properties were calculated using various integral values of the parameter, $n=3$ yields better result. This specific form of the potential with the said value will be applied for calculating the crystal energy and pressure derivative of bulk modulus, $\frac{dB}{dp}$ for rutile-type oxide crystals.

CHAPTER 4

VAN DER WAALS INTERACTIONS

4.1 Origin of van der Waals interaction:

Let us consider two atoms that are gradually brought closer to each other. As long as they remain more than an atomic diameter distance from each other the electronic charge of each atom will tend to shield its own nucleus so that in the zeroth approximation, there will be no net force between the atoms.If we consider more carefully, what happens, however we can see that there should be small residual force. This arises from the fact that the electrons move around in orbits. As a result, the potential produced by any given atom will undergo small fluctuations. This fluctuation will produce small electric fields that polarize the other atoms and create a dipole moment which we denote by M, since the force on M is,

$\vec{F} = (\vec{M}.\vec{\nabla})\ \vec{E}$, where $\vec{E}$ is the electric field and since $\vec{M} = \vec{P}\vec{E}$, where $\vec{P}$ is the polarizability, one obtains,

$$\vec{F} = \vec{P}\,(\vec{E}.\vec{\nabla})\ \vec{E} \qquad (4-1)$$

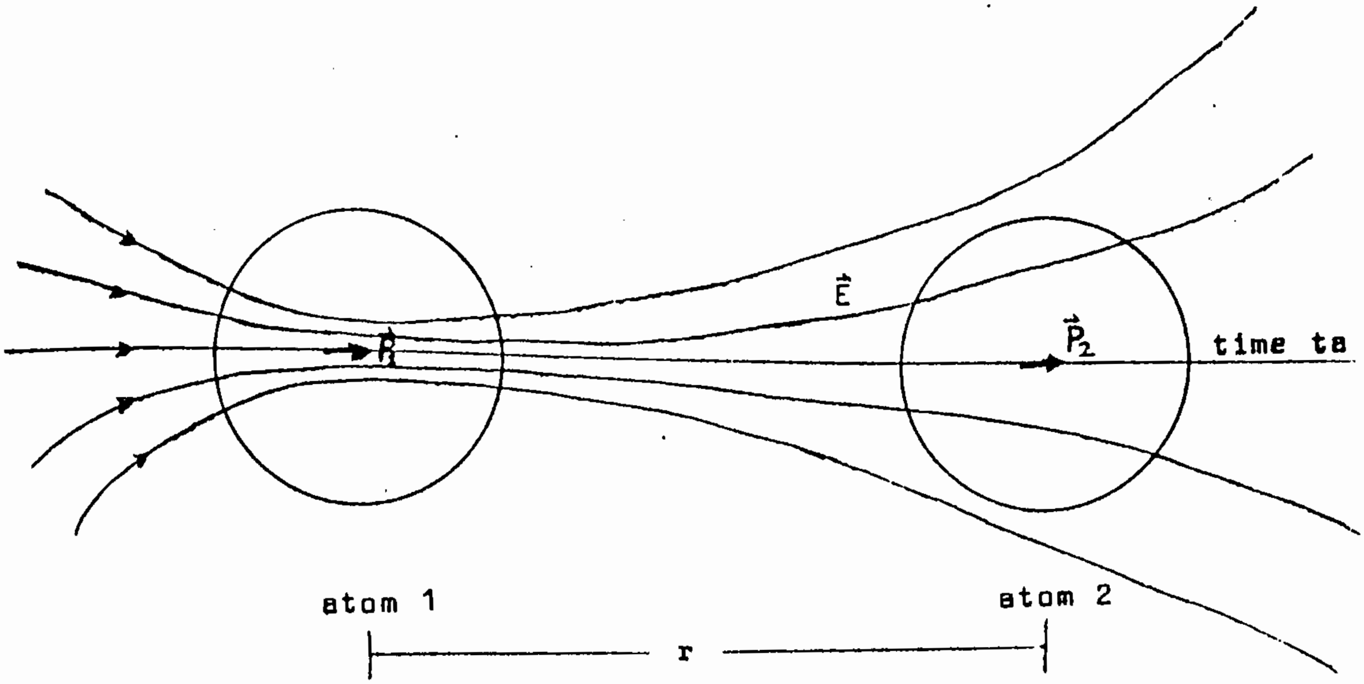
This small residual force is called the van der Waals force[96]. A notable feature of the van der Waals force is that they act between electrically neutral systems and between system having no electric moment, for example, between helium atoms, charge distribution is spherically symmetric so that these atoms have no dipole, quadrupole or higher electric moment. A second important property of these forces is that they are independent of temperature[97]. If the charge distribution on the atoms were rigid, the interaction between atoms would be zero, because the electrostatic potential of a spherically symmetric distribution of electronic charge is cancelled outside a neutral atom by the electrostatic potential of the charge on the nucleus. Then the inert gas atoms could show no cohesion and could not condense, contrary to experiment. It is true that the time-average electric moments are all zero. But the electrons are in motion arround the nucleus even in lowest electronic state, and at any instant of time is likely to be a non-vanishing electric dipole moment from this motion[98]. An instantanuous dipole moment of magnitude P_1 on one atom produces an electric field E of magnitude $2 P_1 / R^3$ at the center of the second atom distance R from the first atom. This field will induce an instantaneous dipole moment $\vec{P}_2 = \alpha \vec{E} = 2P_1/R^3$ on the second atom. Here α is the electronic polarizability defined as the dipole moment per unit electric field.

van der Waals forces have two outstanding characteristics:

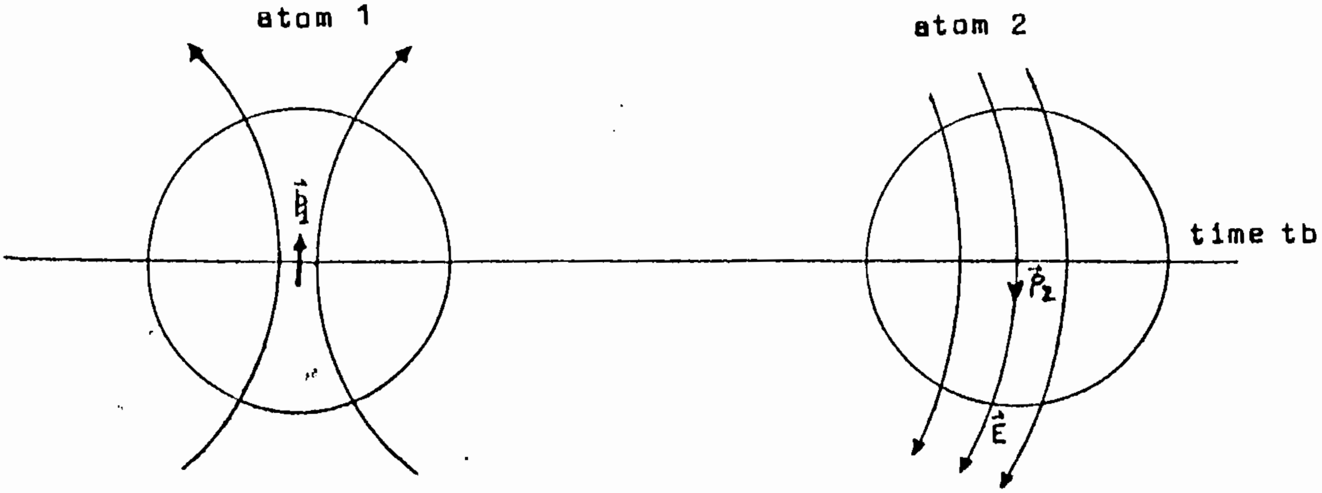
(1) They are much weaker than the forces in chemical bonds.

(2) In many cases, they are additive and can not be saturated. That is, the van der Waals force between two atoms A and B, is not very much affected if energy of say, three neon atoms, Ne_a, Ne_b and Ne_c in a given configuration can be calculated by adding the energy that would be obtained if only Ne_a and Ne_b were present, plus the energy of Ne_b and Ne_c by themslves, plus behaviour of chemical forces. For instance if there are no other hydrogen atoms in the vicinity, the interaction, of two hydrogen atoms, H_a and H_b, is not at all the same as the interaction that occurs when H_b is already chemically bonded to another[99] hydrogen atom H_c.

The van der Waals force is not precisely a two body force since the moment induced in an atom by a second will interact with a third but in the case of neutral atoms it may be regarded as a two-body force for large seperation, when power laws mentioned are valid. In the two-body approximation, it is also central force and it is certainly of short range, so that in general the effect of any but the nearest-neighbours are negligible[100].



(a) Origin of the van der Waals interaction.



(b) At one instant of time, there is dipole moment P_1 on atom 1. This produces an eledtric field E which acquires an induced dipole moment P_2.

Fig. 4-1 : van der Waals interaction between the two inert gas atoms.

The van der Waals potential are short range attractive between closed shell atoms or ions, having an origin connected with correlations of the electronic motions in different atoms. In the case of rare gas solid like $2H^5$,. the van der Waals forces are the sources of binding where their contributions to the binding energy of ionic crystals is small. However, the consideration for producing better aggrement with experimental values of cohesive energies and also for studying various other properties of ionic crystals, for example, the studies on phase transformation, lattice dynamical behaviour and evalution of defect energies require the reliable knowledge of van der Waals potential. The contributions to the van der Waals energy mainly arise from the dipole-dipole (d-d) and the dipole-quadrupole (d-q) interaction. Other higher order terms such as quadrupole-quadrupole (q-q) interaction decay more rapidly with increasing interionic seperation and therefore can be neglected.

Several explanations for van der Waals forces have been proposed. In 1921 Keesom pointed out that if two molecules bear permanent electric dipole moment m_1 and m_2 and if they undergo thermal motion, they will on the average assume orientations leading to attractive force. If R is the vector joining the two dipoles the potential energy of a pair of dipoles is

$$\vec{V} = \frac{1}{|R|^3} \left(\vec{m}_1 \cdot \vec{m}_2 - 3 \frac{(\vec{m}_1 \cdot \vec{R})(\vec{m}_2 \cdot \vec{R})}{|R|^2} \right) \qquad (4-2)$$

Since the thermal motions are subject to the Boltzmann distribution, so that an arrangement whose energy is V has the probability $e^{-V/KT}$, orientations with low energy are favoured on average the quantity $Ve^{-V/KT}$ over all orientation and assuming that KT>>V , it is found that the average potential energy so a pair of dipoles whose seperation is R is approximately

$$V = \frac{2|m_1^2||m_2^2|}{3\,KTR^6} \qquad (4-3)$$

This force evidently decreases in importance as the temperature increases. It is known as the dipole orientation force, or the Keesom force. The (d-d) energy is proportional to $-\frac{C}{r^6}$ i.e. $U_{dd} = -\frac{C}{r^6}$ and the (d-q) energy is proportional to $-\frac{D}{r^8}$ i.e. $U_{d-q} = -\frac{D}{r^8}$

The Van der Waals energy is mainly represented by the relation.

$$U_{vdW} = U_{d-d} + U_{d-q} = - C/r^6 - d/r^8 \qquad (4-4)$$

where C and D are known as the van der Waals co-efficients and R is the interionic separation. The co-efficients C and D are linear combinations of the van der Waals co-efficients (c_{ij}, d_{ij}) for interactions of the various ion pairs weighted by appropriate lattice sums. In the particular case of an ionic crystal formed by two Bravais lattice of ions one has,

$$C = c_{+-} S_{r}^{6} (r_{-}) + \tfrac{1}{2} (c_{++} + c_{--}) S_{r}^{6} (0) \qquad (4\text{-}5)$$

$$D = d_{+-} S_{r}^{8} (r_{-}) + 1/2 (d_{++} + d_{--}) S_{r}^{6} (0) \qquad (4\text{-}6)$$

where r is position vector of the negative ion in the unit cell, the positive ion is being at the origin and the sum[102].

4.2 Derivation of van der Waals co-efficients:

In this section we will consider the derivation of the van der Waals co-efficients c_{ij} and d_{ij}. The following three methods will be discussed in details for obtaining c_{ij} and d_{ij}

i) London-Margenau[103,104](LM) formulation based on the perturbation treatment.

ii) Slater-Kirkwood[105] (SK) treatment based on variational theory.

fii) Kirkwood-Muller[106,107] (KM) formulation.

The expression for the dipole-dipole(d-d) and dipole-quadrupole(d-q) co-efficients obtained from these theories are given below:

LM theory:

$$c_{ij} = 3/2 \alpha_i \alpha_j \frac{E_i E_j}{E_i + E_j} \qquad (4\text{-}7)$$

$$d_{ij} = q/4 \quad \frac{c_{ij}}{e^2} \left(\frac{\alpha_i . E_i}{N_i} \quad \frac{\alpha_j . E_j}{N_j} \right. \qquad (4\text{-}8)$$

SK theory:

$$c_{ij} = 3/2\ \frac{e\hbar}{m^{\frac{1}{2}}}\ \frac{\alpha_i \cdot \alpha_j}{(\alpha_i/N_i)^{\frac{1}{2}} + (\alpha_j/N_j)^{\frac{1}{2}}} \qquad (4\text{-}9)$$

$$d_{ij} = 27/8m\ \frac{\hbar^2 \alpha_i \alpha_j\ (\alpha_i/N_i)^{\frac{1}{2}} + (\alpha_j/N_j)^{\frac{1}{2}\ 2}}{(\alpha_i/N_i) + 20/3(\alpha_i \alpha_j/N_i N_j)^{\frac{1}{2}} + (\alpha_j/N_j)} \qquad (4\text{-}10)$$

MK theory:

$$c_{ij} = -\frac{6mc}{N_0}\alpha_i \alpha_j(\alpha_i/\alpha_i + \chi_j/\alpha_j) \qquad (4\text{-}11)$$

$$d_{ij} = \frac{9mc}{e^2 N_0}\ c_{ij}(\chi_i/N_i + \chi_j/N_j) \qquad (4\text{-}12)$$

where e and m_0 are the charge and mass of an electron, $\hbar$ is the Planck's constant divided by 2π, c is the velocity of light. E_i and N_i are respectively the polarizability, molar susceptibility, characteristic excitation energy and effective number of electrons in ion i. Equation (4-7) to (4-12) have been used by various workers to calculate c_{ij} and d_{ij} in alkali halide and other ionic crystals. These calculations require the knowledge of excitation energies, effective number of electrons and electronic polarizabilities of ions. There are considerable variations in the values of these quantities used in different calculations. A critical discussion along this line is presented in the following section. As far as the soundness of mathematical formulation is concerned, the KM[122,123] equation (3-11) and (4-12) has the great advantage that it does not suffer from uncertainties regarding the off-diagonal term Q_{Kl} defined by Pitzer. On the other hand, the LM and SK theories neglect the contribution of these off-diagonal terms which are not without significance. The KM formulae have been derived in such a manner that off-diagonal terms eliminated with the use of expressions for molar susceptibilities and electron polarizabilities.

4.2.1 Dipole-dipole term, c_{ij}

(a) London formula:

The ground state wave function of the closed shell atom can be written by Slater determinant for N electrons:

$$\Psi = (N)^{-\frac{1}{2}} \quad \det (q_1 , q_2 \cdots q_N) \tag{4-13}$$

To define the polarizability one can write the perturbing potential as:

$$V = F \sum_{p=1}^{N} Z_p \tag{4-14}$$

where F is the electric field along the Z-axis. The variational wave function Ψ' is taken to be

$$\Psi' = \Psi + \sum_{\lambda=1}^{N} a_\lambda \phi_\lambda \tag{4-15}$$

$$\phi_\lambda = (Ni)^{\frac{1}{2}} \quad \det (q_1 , q_2 \cdots \cdots \phi_N) \tag{4-16}$$

$$= Z_\lambda \phi_\lambda f_\lambda \tag{4-17}$$

where f_λ is either unity or a function such as $(1 + C_1 r + C_2 r^2)$. The following three quantities need to be defined as

$$h_\lambda = (\Psi^* | \sum_p Z_p | \phi_\lambda) \tag{4-18}$$

$$\phi_{\lambda\mu} = (\phi_j | H | \phi_\mu) \tag{4-19}$$

$$q_{\lambda\mu} = (\phi_\lambda^* \cdot \phi_\mu) \tag{4-20}$$

Here H is the complete Hamiltonian for the unpertured system and the usual quantum mechanical integrals over all space are indicated.

The energy change up on imposing the field is

$$h' = 2F\sum_{\lambda} a_{\lambda} h_{\lambda} + \sum_{\lambda}\sum_{\mu} a_{\lambda} a_{\mu} \phi_{\lambda\mu} \qquad (4\text{-}21)$$

which is to be minimized with respect to each a_{λ} i.e.

$$\frac{dh'}{da_{\lambda}} = 0 = 2Fh_{\lambda} + 2\sum_{\mu} a_{\mu} \phi_{\lambda\mu} \qquad (4\text{-}22)$$

From the determinant theory, the solution is: $a_{\lambda} = -A_{\lambda}E$ (4-23)

and the minimized energy is: $h' = -F^2 (2\sum_{\lambda} A_{\lambda} h_{\lambda} - \sum_{\lambda}\sum_{\mu} A_{\lambda} A_{\mu} \phi_{\lambda\mu}$

$$= -F^2 \sum_{\lambda} A_{\lambda} h_{\lambda} \qquad (4\text{-}24)$$

The expression for polarizability is:

$$\alpha = -\frac{2h'}{F^2} = 2\sum_{\lambda} A_{\lambda} h_{\lambda} \qquad (4\text{-}25)$$

It is assumed that the q_{λ} are orthogonal to all ϕ_{λ}. This assumption is not necessarily true although the f_{λ} can be selected to make it true. Then

$$q_{\lambda\mu} = 0 \text{ if } \lambda \neq \mu \qquad (4\text{-}26)$$

The calculation of Q is more complex. If f is unity and Hartree wave function are used $Q_{\lambda\lambda} = 1/2$. This value was taken as an approximation by previous workers[103,108]. The off diagonal $Q_{\lambda\mu}$ term which have been neglected previously are not without significance. A_{λ} is given by:

$$A_{\lambda} = \frac{h_{\lambda}}{\sum Q_{\lambda\mu}} \qquad (4\text{-}27)$$

So that $\alpha = 2\sum_{\lambda} \frac{h_{\lambda}^2}{\sum_{\mu} Q_{\lambda\mu}} = \frac{2Nh^2}{\sum Q_{\lambda\mu}}$ (4-28)

Using the above approximations we can get the following expression for the dipole,

$$U_{d-d} = -\frac{6}{R^6}\left(\sum_K \frac{(h_k^A)^2}{\sum_l Q_{kl}^A}\right)\left(\frac{(h_p^B)^2}{Q_{pq}^B}\right)\cdot\frac{(Q_{kl}^A/q_{kk}^A)\cdot(Q_{pq}^B/q_{pp}^B)}{(Q_{kl}^A/q_{kk}^A)+(Q_{pq}^B/q_{pp}^B)} \qquad (4\text{-}29)$$

$$E_A = \sum_l \frac{Q_{kl}^A}{q_{kk}^A} \qquad (4\text{-}30)$$

the equation (4-29) takes the following form

$$U_{d-d} = -\frac{3\alpha_A\alpha_B}{2\,n^6}\,\frac{E_A\cdot E_B}{E_A+E_B} \qquad (4\text{-}31)$$

This formula was first derived by London. The main assumptions in deriving (4-17) are that

(b) (i) all ϕ are orthogonal to ψ_λ

(ii) $f_\lambda = 1$ and (iii) off-diagonal terms $\phi_{\lambda\mu}$ do not contribute to polarizability and dipole-dipole energy.

The assumption lead to the following results:

$$q_{\lambda\lambda} = h_\lambda = \langle \phi_\lambda^* \; z_\lambda^2 \; \phi_\lambda \rangle \qquad (4\text{-}32)$$

so that we have;

$$\alpha_A = 2\sum_\lambda \frac{h_\lambda^A}{E_A} = \frac{2\,Nh^4}{E_A} \qquad (4\text{-}33)$$

From equation (4-30) and (4-33) we get,

$$E_A^{-1} = \frac{h^A}{\sum_l Q_{kl}^A} = \left(\frac{\alpha_A}{2n\sum_l Q_{kl}^A}\right) \qquad (4\text{-}34)$$

Inserting (4-34) in (4-31) and assuming that off-diagonal terms do not contribute i.e. $\sum Q = \frac{1}{2}$, we get,

$$U_{d-d} = -3/2\,\frac{\alpha_A\alpha_B}{R^6}\,(\alpha_A/N_A)^{\frac{1}{2}} + (\alpha_B/N_B)^{\frac{1}{2}} \qquad (4\text{-}35)$$

which is the SK formula for the van der Waals dipole-dipole interaction.

(c) KM formula

Another useful equation for the dipole-dipole energy is that obtained by Kirkwood[106] and Muller[107]. This contains the diamagnetic susceptibility as well as the polarizability per atom of a spherically symmetric system is given by:

$$\alpha = -(2 m c^2)^{-1} \Sigma_k (Z_k^2)^2 \qquad (4\text{-}36)$$

In view of electronic arrangement we can for a sub-shell of equivalent electrons

$$\alpha_A = -\frac{Nh^4}{2 m c^2} \qquad (4\text{-}37)$$

Equations (4-36) and (4-37) imply that the assumption that the same number of electrons contribute to polarizability as to susceptibility. Such an assumption has been found to be fairly satisfactory. Thus we have,

$$E_A^{-1} = -(4 m c^2)^{-1} \left(\frac{\alpha_A}{\chi_A} \right) \qquad (4\text{-}38)$$

Then the dipole-dipole energy then becomes

$$U_{d-d} = -\frac{6 m c^2}{N_O R^6} \chi_A \chi_B \left[\left(\frac{\chi_A}{\alpha_A} + \frac{\chi_B}{\alpha_B} \right) \right]^{-1} \qquad (4\text{-}39)$$

In equation (4-39), N_o is the Avogadro's number and χ is now the molar susceptibility in cm^3. The most remarkable feature in deriving (4-39) is that $\sum Q$ has been eliminated. Thus the Kirkwood-Muller formula (4-39) has the great advantage that it does not suffer from the uncertainties regarding the off-diagonal term Q_{kl}.

4.2.2 Dipole-quadrupole term d_{ij}

To derive the SK theory of the type:

$$d_{ij} = \frac{27}{8m} h^2 \frac{\alpha_i \alpha_j \left((\alpha_i / N_i)^{\frac{1}{2}} + (\alpha_j / N_j)^{\frac{1}{2}} \right)^2}{(\alpha_i / N_i) + 20/3((\alpha_i/N_i)(\alpha_j/N_j))^{\frac{1}{2}} + (\alpha_j/N_j)}$$

let a system have the ground state wave-function with energy E_o

for the unperturbed Hamiltonian H i.e.

$$H_o \Psi_o = E_o \Psi_o \qquad (4-40)$$

Let the perturbed Hamiltonian be H whose

$$H = H_o + V \qquad (4-41)$$

We assumed that the perturbed wave-function closely approximated be a function of the form,

$$= \Psi_o (1 + V) \qquad (4-42)$$

where V is small compared to unity. From the variational theorem in quantum mechanics, the excess energy of the system arising from the perturbation approximation closely reduces of the value.

$$E = \langle H \rangle - E_o \qquad (4-43)$$

$$= V_{oo} + 2(vV)_{oo} + \frac{h^2}{2} \sum_{\substack{i \\ \text{co-ords}}} \frac{1}{m_i} \left(\left(\frac{dv}{dx_i} \right)^2 \right)_{oo}$$

where the summation goes over all the electrons and over the three co-ordinates for each electron.

Using the above formula, the polarizability of an atom can be derived to be

$$\alpha = 4me^2/9h^2 \; N(r^2)^2_{oo} \qquad (4-44)$$

From the multiple expansion of the charge distribution in two atoms we get the dipole-quardrupole interaction potential of the two atoms to be

$$V = 3/2 \; e^2/r^4 \sum_{ij} (r_{1i}^2 \; z_{2j} - z_{1i} \; r_{2j}^2 + (2x_{1i} x_{2j} + 2y_{1i} y_{2j} - 3 \; z_{1i} z_{2j} (z_{1i} - z_{2j}) \qquad (4-45)$$

where the subscripts 1,2 refer to electrons in the first and second atom and i,j goes from 1 to N,N the respective numbers of electrons participating in the interaction.

We use the first approximation in Hasse's[109] method and express v as

$$V = v = ((r_{1i}^2 Z_{2j} - Z_{1i} r_{2j}^2 + 2x_{1i} \quad x_{2j} + 2y_{1i} \quad y_{2j} - 3 Z_{1i} \quad Z_{2j}) \quad (Z_{11} - Z_{2j}) \qquad (4\text{-}46)$$

where λ is an undetermined multiplier.

It is determined the matrix elements in (4-43) that,

$$V_{oo} = 0 \qquad (4.47)$$

$$v_{oo} = 0 \qquad (4\text{-}48)$$

Also $(vV)_{oo} = \frac{2e^2}{3r^4} \quad N_1 \; N_2 ((r_1^4)_{oo} (r_2^2)_{oo} + (r_1^2)_{oo} (r_2^4)_{oo}$ (4.49)

From equation (4-46) we have

$$\frac{dv}{dx_{1k}} = \lambda \sum_J \quad (2x_{1k} \quad Z_{2j} + 2x_{2j}(Z_{1k} - Z_{2j})) \qquad (4\text{-}50)$$

i.e. $\left(\frac{dv}{dx_{1k}} \right)^2_{oo} = \lambda^2 N_2 \; (8/9(r_1^2)_{oo} (r_2^2)_{oo} + 4/15 \; (r_2^4)_{oo})$ (4-51)

Thus we obtain for the kth electron of the first atom

$$\sum_{\text{co-ords}} \left(\frac{dv}{dx_{1k}} \right)^2_{oo} = \lambda^2 N_2 \, (40/9(r_1^2)_{oo}(r_2^2)_{oo} + 4/3(r_2^4)_{oo} \;) \qquad (4\text{-}52)$$

Finally summing over all the electrons of the first atom and adding a symmetrical term for the second atom we have

$$\left(\frac{dv}{dx_1} \right)^2_{oo} = \lambda^2 N_1 \; N_2 (\; 4/3 \; (r_1^4)_{oo} + 80/9(r_1^2) \quad (r_2^2)_{oo} + 4/3 \; (\quad r_2^4 \quad)_{oo} \;) \qquad (4\text{-}53)$$

Substituting (4-54,) (4-48), (4-49) and (4-43) we have the perturbation energy to be

$$E = \frac{4e^2}{3r^4} \quad N_1 \; N_2 ((r_1^4)_{oo} (r_2^2)_{oo} + (r_1^2)_{oo} (r_2^4 \quad)_{oo})$$

$$+ \frac{h}{2m} N_1 N_2 (4/3 (r_1^4)_{oo} + 80/9 (r_1^2)_{oo} (r_2^2)_{oo} + 4/3 (r_2^4)_{oo})^2 \qquad (4\text{-}54)$$

The result (4-54) contains the undetermined multiplier To eliminate it we minimize (4-54) with respect to λ we then get the dipole-quadrupole interaction energy as:

$$\Delta E_{dq} = - \frac{d}{r^8} = - \frac{Z\, me^4}{9h^2 r^8} N_1 N_2 \frac{((r_1^4)_{oo} (r_2^2)_{oo} + (r_1^2)_{oo} (r_2^4)_{oo})^2}{(4/3 (r_1^4)_{oo} + 80/9 (r_1^2)_{oo} (r_2^2)_{oo} + 4/3 (r_2^4)_{oo})} \qquad (4\text{-}55)$$

From equation (4-44) we can express r^2 in terms of the polarizability

as: $$(r^2)_{oo} = \left(\frac{9 \hbar^2}{4\, me^2} \right)^{\frac{1}{2}} \left(\frac{\alpha}{N} \right)^{\frac{1}{2}} \qquad (4\text{-}56)$$

We also make the approximation that

$$(r^4)_{oo} = (r^2)^2_{oo} \qquad (4\text{-}57)$$

which is reasonably valid whenever the electrons are distributed in a shell around the nucleus with a strong speaking of the electron density at some radius. Substituting (4-56) and (4-57) in (4-55) we thus obtain the following formula for the dipole-quadrupole interaction co-efficient.

$$d_{12} = \frac{27h^2}{8\ m} \alpha_1 \alpha_2 \frac{((\alpha_1 / N_1)^{\frac{1}{2}} + (\alpha_2 / N_2)^{\frac{1}{2}})^2}{(\alpha_1 / N_2) + 20/3 (\alpha_1 \alpha_2 / N_1 N_2)^{\frac{1}{2}} + (\alpha_2 / N_2)} \qquad (4\text{-}58)$$

4.3.1 Origin Of polarizability :

In order to understand the origin of polarizability of an atom let us first define dipole moment and local electric field.

The dipole moment of the pair of charge ±q is $\vec{P}$ =

$q\vec{r}_1 - q\vec{r}_2 = q\vec{R}$, and is directed from the negative charge toward the positive charge. The local electric field at an atom is the sum of the electric field E_o from external sources and of the field of the dipoles within the specimen, we write,

$$E_{local} = E_0 + E_1 + E_2 + E_3 \qquad (4-59)$$

The contribution of the local field are as given in figure 4-2.

The polarizability of an atom is defined in terms of the local electric field at the atom:

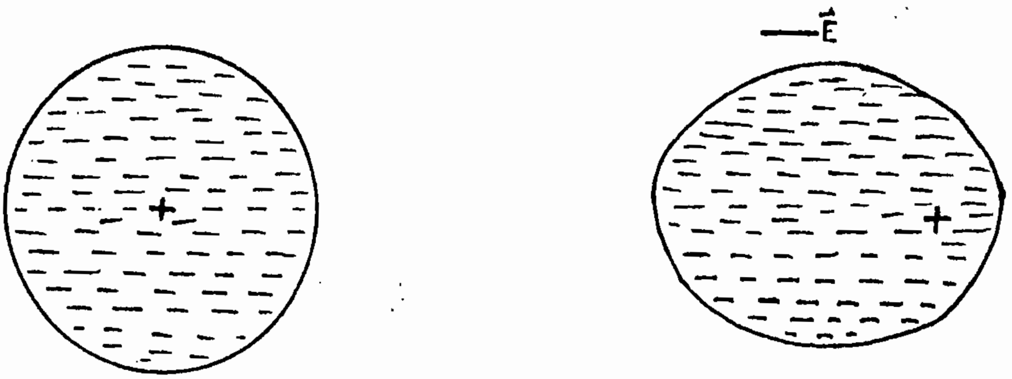
$$P = E_{local} \qquad (4-60)$$

where P is the dipole moment. The polarizability is an atomic properties,but the dielectric constants will depend on the manner in which the atoms are assembled to form crystal. The polarizability has the dimension of $(\text{Length})^3$. The total polarizability may be seperated into three parts:

i) Electronic,

ii) Ionic and (iii) Dipolar,

The electronic polarizability arises from the displacement of the electronic shell relative to a nucleus. The ionic contribution comes from the displacement of a charged ion with respect to other ions. The dipolar polarizability arises from molecules with a permanent electronic dipole moment that can change orientation in

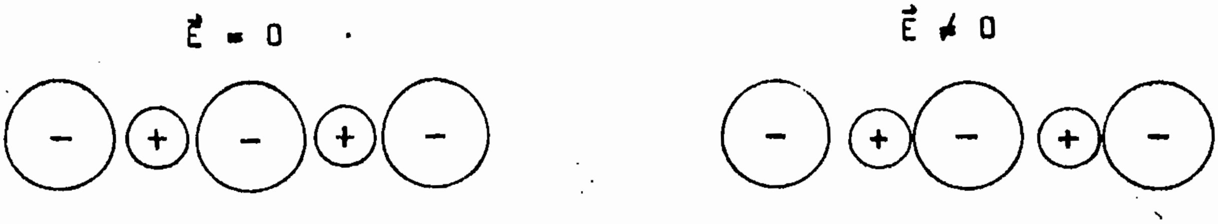


Unpolarized atom

Polarized atom

Fig. 4-2 : Polarized and unpolarized atoms.

(a) Electronic



(b) Ionic

(c) Dipolar

Fig. 4.3 : Different polarizabilities.

an applied electric field. The contributions to the polarizability are as given in figure 4-3.

Let us now calculate the polarizability of an ionic crystal. The polarizability of molecules plays an important role in several of the theories of long range intermolecular forces. Accordingly we devote this section to a discussion of the calculation of polarizability. First the general quantum mechanical theory is presented and this theory is applied to the calculation of the polarizability of molecule. Then the principle of additivity of polarizability is discussed and finally the use of screening constants to calculate polarizability and other molecular properties is considered.

4.3.2. Polarizability versus ion-environment:

The polarizability of an ion is sensitive to its environment. For example, the best spectroscopic value for polarizability of the lithium ion is 0.0283 $\AA^3$ and the most recent theoretical estimation for the polarizability of the free fluoride ion are 1.56 and 1.40 $\AA^3$. The sum of these lies between 1.59 and 1.43 $\AA^3$ whereas the experimental polarizability per ion pair in crystalline LiF is 0.915 $\AA^3$.

The existence of such effects was demonstrated in principle over 40 years age by Spangenberg[110] who showed that the polarizability per ion-pair in crystalline alkali halides cannot be accurately described as sums of constant polarizabilities for the component ions. This is illustrated by the fact that the difference in polarizability between NaF and NaBr is 3.24 $Å^3$ whereas the corresponding difference in the rubidium salts is 3.43 $Å^3$.

Fajans and joos[111] proposed on the basis of quite general arguments that the polarizability of a positive ion is increased in the Coulomb field on an anion, while the polarizability of a negative ion should be decreased in the Coulomb field of a cation. In an extensive review of the information available at the time, they applied these idea to correlate not only the polarizability of ionic component in crystals and in solution but also those of molecule composed of groups differing substantially in electronegativity. The application of these concepts to a great variety of substances has been pursued subseqently by Fajans and his collaboraters in a long series of publications[112,113]. Fajans and Joos also proposed a formalism for estimating the polarizability of the free ions, both positive and negative, on the basis of two qualitative rules:

(1) $\alpha^+/\alpha^0 > \alpha^0/\alpha^-$ where the subscripts positive, 0, negative refer to monoatomic cation, noble gas and anion in an isoelectronic series and (2) $(\alpha^+/\alpha^0)_n < (\alpha^+/\alpha^0)_{n+1}$ where n is the principal quantum number of the balance shell in an isoelectronic pair. These rules together with experimental values for the polarizabilities α^0_n, independent estimates of α^+ for the lighter cations and plausible assumptions about the trends in the inequalities in rules (1) and (2), led to estimates for the polarizabilities of the ions. These estimates were influenced also by the estimated polarizabilities[111] of the heavier anions in aqueous solution; with minor modifications, they are current to day[114]. They appear to have had a significance influence on the selection of parameters for Pauling's semi empirical calculation[115] of the polarizabilities of the free alkali halide ions.

Despite the evidence summarized above that ionic polarizabities vary with environment, many workers have based their estimates of polarization energies and London energies in ionic system on the "Constants" or additive ionic polarizabilities assigned by Tessman, Kahn and Shockley[116]. These values were chosen to minimize the mean square deviations from additivity in the polarizabilities of ionic crystals, but with due to consideration of independent estimates of the polarizabilities of the ligther free alkali ions, especially Li^+. Clearly the use of these additive polarizabilities must be regarded as only a first approximation. More realistic estimates of the secondary interactions in ionic systems could be made if reliable values were available for ionic polarizabilities in different environments. Indeed the values deduced by TKS for the polarizabilities of the oxide ion, O^{2-} in a number of crystals ranged from 0.9 to 3.2 $Å^3$, illustrated again the existence of a substantial environmental effect.

At the level of approximation represented by the lightly succesful Born-Mayer model[2] of ionic crystals, it is neutral to represent the polarizabilitity of an ionic crystal as the sum of anionic and cationic component polarizabilities. From the point of view of the quantum mechanical description of the system, however, this procedure can not be strickly justified. The nature and validity of the quantum mechanical approximations involved in this additivity concepts have been discussed by Ruffa[117]. Making use of a well established description of the polarizabilities of an atom or ion as proportional to a weighted mean square excitation energy, Ruffa extended his analysis to carry out what amounts to a semi-quantitative of the hypothesis of Fajans & Joos. On the basis of a some what intuitive estimates of the effects of the lattice interactions on the mean-square excitation energy, he confirmed their contention that the polarizability of a cation is increased by lattice interactions, whereas the polarizability of an anion is decreased even more. As Ruffa himself admits, however, some of the parameter that entered his theory could be estimated only roughly and his estimates of the magnitude of the changes in polarizability may have been too large. In addition, he based his estimates of the mean square excitation energies of the unperturbed ions on Pauling's estimates of the free ion-polarizabilities. As will be shown below, subsequent work has made available more reliable estimates for the polarizabilities of the lighter ions in the free states and has raised doubts about the accuracy of Pauling's estimates for the polarizabilities of the heavier ones.

The effect of lattice interaction on the polarizabilities of the component ions in the chlorides and fluorides of lithium, sodium & potassium has also been analyzed by Mitskevich[118] on basis of variation theory. His treatment leads to the same qualitative conclusions that the polarizabilities of the ions is increased in the crystal and that of the negative ions is decreased relative to the values that characterize the free ions.

Pentrashen, Abarenekov and Krostofel[119]have presented a model which allows for the modification of the Hartreefock distribution by the Madelung potential. The expected dilution of the cation and construction of the anion were demonstrated. The corresponding perturbations of the polarizabilities have been investigated by Ledovskaya[120]. Qualitative similar results have been obtained by Paschalis and Weis[121] using the model of an ion embedded in a hollow sphere, a sphere which carries an electric charge of the same magnitude but opposite in sign to that of the ion considered.

Wilson and Curtis have treated the variation of anion polarizabilities in the alkali halides using the model of a compressible conducting sphere. They assume that the relative decrease of the polarizability experienced by the anion is proportional to the compressive force acting upon the anion. This force was approximated by the Coulomb force. Applying their model to the alkali halides having the sodium chloride structure, they found free anion polarizabilities that were essentially equal to the cube of the anion radii. The refractive index data did not seem to require signifiant enhancement of the cation polarizabilities.

Pirenne and Kartheuser[122] have obtained a set of free ion polarizabilities that is based on the presumtion that crystal polarizabilities are enchanced by a dipole-dipole interaction. Some theoretical support for this position, which contradicts Fajans principle, is given by Heinrich.

An alternative approach to this problem was made earlier by Burns and Wikner[124], who calculated the polarizabilities of the fuloride ion from the approximate wave functions proposed by Yamashita[125] for the free ion and for the fluoride ion in the crystal of LiF. They obtained a polarizability of 1.31 Å^3 for the free ion but a smaller polarizability of 1.11 Å^3 for the contracted wave function, of the fluoride ion in the crystal. The model which we present below is related conceptually to the results of these calculations.

A model for the polarizability of anion in crystals:

This model can be based on the following arguments. The major contribution to the polarizabilities of a closed shell atom or ion is made by the electrons of its highest occupied sub-shell. In the halides ions these electrons and relatively weakly bound and might therefore be expected to respond to a polarizing field rather as if they were the electrons of a conduction sphere. Classically the polarizabilities of a conducting sphere is the cube of its radious. In applying this concepts to a halide ion, it is not clear how the radius should be chosen. We shall defer cosideration of that question until a later section; for the moment, we simply assume that the polarizability of an anion responds to its environment as if it were propotional to a radius cubed i.e. to a volume.

We would not except this model to apply as well to the polarizabilities of cations and of the noble gases since the ionization potentials of these systems are much lighter than those of the halide ions. That one should not except a proportionality between polarizability and volume in general is shown by the from of the of these well known quantum theory expressions for one electron polarizability as the square of a sum of terms of the form,

$$\langle \mu_i r_i^2 \mu_i \rangle \text{ and } |\langle \mu_i \, r_i \, \mu_j \rangle|^2 \qquad (4\text{-}61)$$

where r_i is the radius from the nucleus to the ith electron is the corresponding one electron wave function. In a condensed phase we assume that an increment dF of the compressive force results in a proportionate decrease of the polarizability, similar to the decrease in effective volume. Thus we write for the ith ion

$$d\alpha_i = -K_i \alpha_i F_i \qquad (4\text{-}62)$$

where K_i is the constant analogous to a compressibility. Integration yields

$$(\ln \alpha_i = \ln \alpha_i^0 - K_i F_i \qquad (4\text{-}63)$$

where α_i^0 is the polarizability of the free ion.

Let us approximate the lattice free energy U of a crystal as a sum of the coulomb term and a repulsive potential , we ignore for the moment the K.E. and entropy terms and the London potentials. The use of a more elaborate model will be discussed in a later section. Thus we write

$$U = -\frac{\alpha e^2}{r} + \phi(r) \qquad (4\text{-}64)$$

where α is the Madelung constant. At the equilibrium nearest neighbour distance, r_e

$$\left(-\frac{dU}{dr} \right) = \alpha e^2/r_e^2 + \phi'(r_e) = 0 \qquad (4\text{-}65)$$

Here the attractive and repulsive forces acting on the ions are in balance and we may write for the compressive force $F(r_e)$

$$F(r_e) = -\phi'(r_e) = \alpha e^2/r_e^2 \qquad (4\text{-}66)$$

Then equation for correlating ionic polarizabilities between different crystals with the same structure because

$$\ln \alpha_i = \ln \alpha_i^o - K_i \kappa_e e^2/r_e^2 \quad (4-67)$$

or $$\log \alpha_i = \log \alpha_i^o - b/r_e^2 \quad (4-68)$$

we have ignored the difference between the compressive forces acting on ions of differing "size".

Model - 1

It was assumed that the polarizabilities of Li^+ and of Na^+ remain constant at their well-known vaccum values of 0.0283 and 0.148 $\mathring{A}^3$, respectively. In each of the lithum and sodium salts the polarizability of the halide ion was obtained by subtracting the polarizability of the cation, assumed to be constant, from the polarizability per ion pair of the salt. These anion polarizabilities were extrapolated by means of equ. (4-68) to the values of r_e^{-2} for the corresponding potassium salts and the polarizability of the potassium ion was obtained for each salt by differnce. The values obtained for $\alpha(K^+)$ ranged from 0.75 to 0.84 $\mathring{A}^3$ with no obvious trend with r_e^{-2} it was therefore assumed that $\alpha(K^+)$ was approximately independent of r_e^{-2}. The average value was 0.787 $\mathring{A}^3$ with an average deviation of 0.024 $\mathring{A}^3$; this value was used to $\alpha(\bar{X})$ at the values of r_e^{-2} obtaining in the potassium salts. These from the lithium and sodium salts to extrapolate to r_e^{-2} for the rubidium salts. The values of $\alpha(Rb^+)$, obtained as before ranged from 1.31 to 1.36, and again showed no systematic trend with r_e^{-2} ; the values obtained from fluoride and iodide salts were almost identical. The average value of $\alpha(Rb^+)$, 1.328 Å^3 with an average deviation of 0.015 Å^3 was then used as before to obtain $\alpha(Cs^+)$ in CsF. Here the value obtained was 2.31 Å^3.

Model - II: Variable cation polarizability.

It is very likely that the polarizabilities of the alkali cations are larger in ionic crystals than in free space. The magnitude of the increase is far from certain, however, since the increase resulting from electrostatic effects is opposed by the repulsive interactions with neighbouring ions.

The approximation poroposed by Ruffa for the polarizability of a cation in a crystal can be written in the form

$$\alpha_0^+/\alpha_c^+ = (1-2.434\,\alpha_0^{1/2} / n^{1/2}\cdot r_e)^2 \qquad (4\text{-}69)$$

where α_0^+ is the free-ion polarizability, n is the total number of electrons in the ion, and r_e is the nearest neighbour anion-cation distance. This expression has been used to calculate cation polarizabilities in the alkali halides on the basis of the spectroscopic estimates of the free-ion polarizabilities rather than the Pauling estimates used by Ruffa. The resulting values for K^+, Rb^+ and Cs^+ though smaller than Ruffa's, appeared still to be much too large on the basis of the values obtained by difference for the polarizabilities of the anions in the crystals. Thus for example in the fluorides, the resulting value of $\alpha(F^-)$ increased as expected from LiF to NaF but then declined through the salts of K^+ and Rb^+ to unreasonably low value of 0.23 $Å^3$, in CsF. It therefore appeared likely that overestimates also the polarizabilities of Li^+ and Na^+ in their salts.

In the "bootstrap" procedure, it has been assumed that the functional form provides a reasonable approximation for interpolation or extrapolation with respect to r, but it has been used for this purpose in the following empirical form, in which C is a constant characteristic of the ith cation

$$\left(\frac{\alpha_o}{\alpha_c} \right)^{1/2} = 1 - \frac{C_i}{r_e} \qquad (4-70)$$

For the range of values of C_i which has been found useful to describe the experimental data is very closely approximated by

$$\alpha_c^+ = \alpha_o^+ e^{2C/r_e} \qquad (4-71)$$

Sum rule analysis of free ion polarizabilities:

First an analysis of the polarizability of a system of non interacting free ions will be made. Considering one of the isolated ions for the moment, its static electronic polarizability may be obtained directly from the quadratic Stark effect since at ordinary temperature the ground state of the ion is the only one having an appreciable probability of being occupied. If the electric field is in the x direction, second order perturbation theory yields for the polarizability, the results.

$$\alpha = 2e \Sigma_{\gamma'} |\langle \gamma' | x | \gamma \rangle|^2 / E_{\gamma'\gamma} \qquad (4\text{-}72)$$

where $X = \sum_i x_i$, the x_i being the x co-ordinates of the individual electrons and $E_{\gamma'\gamma} = E_{\gamma'} - E_{\gamma}$. There is no first order contribution since for free ions $\langle \gamma | x | \gamma \rangle = 0$. Evaluation of the expression (4-72) is complicated by the fact that it requires a knowledge of the energies and wave functions of all the states of the system, which is generally no available. Consequently, it is necessary to know the wave functions as well as the specific energies of all the quantum states.

Such a means is available in this case in the form of a sum rule which was discovered independently by Thomas and from a consideration of the dispersion formula for optical frequencies from the standing point of the corresponding principle. It follows directly from the commutation relations

$$[q_i , p_i] = i\hbar_{ij} \qquad (4\text{-}73)$$

for the electronic co-ordinates and momenta and may be written in the following manner:

$$(8\pi^2 m/h^2)\sum_{\gamma'} E_{\gamma'\gamma}\left|\langle\gamma|\,x\,|\gamma'\rangle\right|^2 = n \qquad (4-74)$$

where n is the number of electron in the ions. Identical relations hold for

$$Y = \sum_i y_i \quad \text{and} \quad Z = \sum_i z_i$$

The use of (4-40) enables one to express (3-38) as

$$\alpha = (2e^2/\vec{E}_1^2)\sum_{\gamma'} E_{\gamma'\gamma}|\langle\gamma|x|\gamma'\rangle = e^2 h^2 n/4\pi^2 m\,\vec{E}_1^2 \qquad (4-75)$$

where $\vec{E}_1$ is a parameter whose magnitude is determined by the equlity of the right hand sides of (4-72) and (4-75). Because the sum rule is identical for all three co-ordinates, the polarizability is independent of the direction of the field. Moreover, it may be seen that the expression for α has been reduced to a dependence upon only one unknown parameter i.e. $\alpha \propto \frac{1}{\vec{E}_1^2}$. The quantity $\vec{E}_1$ may be loosely reffered to as being a mean excitation energy although this designation is not a precise one since the values of such quantities are dependent upon the sums from which they are obtained.

This fact may be illustrated by obtaining an expression for the polarizability in another way. The sum rule (4-75) may be simplified by taking advantage of the matrix sum rule,

$$\sum_{\gamma'\gamma}|\langle\gamma|\,x\,|\,\gamma'\rangle|^2 = \langle\gamma|\,x^2|\gamma\rangle - |\langle\gamma|\,x|\,\gamma\rangle|^2 \qquad (4-76)$$

to yield the following:

$$\begin{aligned}(8\pi^2 m/h^2)\,\vec{E}_2^{x}\langle\gamma|\,x^2|\gamma\rangle &= n\\ (8\pi^2 m/h^2)\,\vec{E}_2^{Y}\langle\gamma|y^2|\gamma\rangle &= n\end{aligned} \qquad (4-77)$$

$$(8\pi^2 m / h^2)\ \vec{E}_2^{\,z} \langle r | z^2 | r \rangle = n$$

where advantage has been made of the fact that $\langle r | X | r \rangle = \langle r | Y | r \rangle\ \langle r | Z | r \rangle = 0$, and where $\vec{E}_2^{\,x}$, $\vec{E}_2^{\,y}$, $\vec{E}_2^{\,z}$ are parameters whose magnitudes are determined by the equality of the left hand sides of (4-74) and (4-77).

Equations (4-77) may be simplified further by the use of the principle of spectroscopic stability. According to this principle, sums of the form $\sum_{m,m'} |\langle nm | A_q | n'm' \rangle|^2$, Where m is a space quantization index, are independent of the axis of the quantization so that

$$\sum_{m,m'} |\langle nm | A_q | n'\ m' \rangle|^2 = \sum_{n',m'm} |\langle n\ m | Ay | n'\ m' \rangle|^2 = \sum_{n',m',m} |\langle n\ m | A_Z | n'\ m' \rangle|^2$$

In this case, the result is

$$\sum_{r' \neq r} |\langle r | X | r' \rangle|^2 = \sum_{r' \neq r} |\langle r | Y | r' \rangle|^2 = \sum_{r' \neq r} |\langle r | Z | r' \rangle|^2$$

Consequently, equations (4-77) reduce to

$$(8\pi^2 m / h^2)\ \vec{E}_2 \langle r | \left\{ \begin{matrix} X^2 \\ Y^2 \\ Z^2 \end{matrix} \right\} | r \rangle = n \tag{4-78}$$

where the $\vec{E}_2'$s have been replaced by $\vec{E}_2$. In a similar manner, one may define as $\vec{E}_3$ given by

$$\vec{E}_3 = 2e^2 \langle r | X | r \rangle \tag{4-79}$$

So that we have as a second expression for

$$\alpha = 2e^2\ n\ c / \vec{E}_2 \cdot \vec{E}_3 \tag{4-80}$$

where $c = \frac{h^2}{8\pi^2 m}$. The result is again independent of direction in agreement with (4-75). The quantities $\vec{E}_1$, $\vec{E}_2$ and $\vec{E}_3$ which may be called the mean excitation energies of the first, second and third kinds respectively, satisfy the relationship,

$$\vec{E}_1^{2} = \vec{E}_2 \cdot \vec{E}_3 \qquad (4\text{-}81)$$

Although they are not equal, one might generally expect them to be of the same order of magnitude. A specific comparison of these quantities is made by the relation

$$\frac{\alpha_1}{\alpha_2} = \left(\frac{R_1^4 n_2}{R_2^4 n_1} \right) \left(\frac{\bar{E}_2^2(1) / \bar{E}_1^2 (1)}{\bar{E}_2^2 (2) / \bar{E}_1^2 (2)} \right) \qquad (4\text{-}82)$$

A system of non-interacting free ions is electric dilute so that the effective and applied fields acting on a given ion are the same. Under these conditions, the polarizability of the system, is the sum of the ionic polarizabilities, and is equal to the total polarization divided by the applied field. If

$$X = \sum_{i=1}^{N} x_i = \sum_{i=1}^{M} x_i$$

where N is the number of electrons in the system and M is the number of ions, then

$$\begin{aligned}\alpha_S = \sum_{i=1}^{M} \alpha_i &= 2e^2 \sum_{r'} \left| \langle r | \; x | r' \rangle \right|^2 / E_{r,r'} \\ &= 2e^2 \sum_{i=1}^{M} \langle r | \; x_i^2 | r \rangle / \vec{E}_{3i} = (2e^2/\vec{E}_{3S}) \sum_{i=1}^{M} \langle r | \; x_i^2 | r \rangle \\ &= 2e^2 \; C \sum_i (n_i \; / \vec{E}_{1i}^{2} \;) \qquad (4\text{-}83)\end{aligned}$$

where $\vec{E}_{3S}$ is the mean excitation energy of the third kind for the system. It is evident that

$$\vec{E}_{3S} = 2e^2 \sum_{i=1}^{M} \langle r | x_i^2 | r \rangle / \sum_{i=1}^{M} \alpha_i = \sum_{i=1}^{M} \alpha_i \vec{E}_{3i} / \sum_{i=1}^{M} \alpha_i \qquad (4\text{-}84)$$

Because there is some ambiguity in the value of the mean excitation energy, it is dangerous to attempt to determine polarizabilities by estimating E's. However, the value of (4-75) and (4-82) to our approach to the determination of the polarizabilities of ions in crystal lies in calculating E's directly from theoretically determined free ion values. Then given a crystalline environment in which the ions maintain their individuality to good approximation and the crystalline interaction is known to the extent that the change in the E's from their free ions values may be estimated, values for the ionic polarizabilities may be obtained. The electronic polarizabilities of ions alkaline earth chalcogenides were obtained by Tessman et.al.[116] by performing an analysis of the crystal refraction data on the basis of the Lorentz-Lorentz relation employing the additivity rule. The electronic polarizabilities of ions in alkaline earth chalcogenides crystals obtained by Tessman et.al. may by Boswarva[68] differ from free state values (Fajans and Joos), (Pauling), being larger for cations and smaller for anions.

When the ions are transported from free state to a crystal, their polarizabilities are changed. According to Ruffa[117] one can write

$$\frac{\alpha_c^+}{\alpha_f^+} = \frac{E_{f+}^2}{E_{c+}^2} \qquad (4-85)$$

where $E_{c_+} = E_{f_+} - eV_M$. α_{f_+} and α_{c_+} are respectively the free state and crystalline state polarizabilities of a cation. V_M is the Madelung potential, E_f is the energy parameter defined as

$$E_{f}^{2} = \frac{e^{2}\hbar^{2}n}{m\alpha_{f+}} \qquad (4\text{-}86)$$

where e and m are the electronic charge and mass respectively. n is the number of electrons in the ion. $\hbar$ is the Planck's constants diveded by 2π . An equation similar to (4-85) cannot, however, be used for anions because of the excitation levels to the anion polarizabilities in the crystal which has no counterpart in free state. In addition, quantum states above the first ionization continum contribute substantially to the free anion poalrizabilities. Ruffa therefore obtained a different expression for anion polarizabilities which is as follows

$$\frac{\alpha_{c^-}}{\alpha_{f^-}} = \frac{E_{f^-}^{2}}{E_{c^-}^{2}} \qquad (4\text{-}87)$$

where α_{c^-} and α_{f^-} are the crystalline and free state polarizabilities of anion, E_{f^-} is the energy parameter analogus to E_{f+} . Crystalline state parameter E_{c^-} is

$$E_{c^-} = \frac{1}{4}((\Delta - e^{2}/R) + 3(E_{f^-} + \Delta - E))$$

where $= 2e(V_M - V_R) + E - I + Q$ (4-88)

where R is the interionic seperation, e V_R is the repulsive energy, E the electron affinity of anion, I the ionization potential of cation and Q is the energy of interaction between the free atoms and the crystal environment.

4.3.3 Methods for the calculation of polarizabilities: Variational procedure of screening constant method:

The polarizability of a molecule can be approximated by Hyllerrss[126] and Hasse[109]. Let us consider an unperturbed molecule containing n electrons and nuclei for which the quantum mechanical Hamiltonian operater is H_0. The energy of the molecule in its ground state is designated by E_0. Associated with this energy is a wave function ψ_0, which satisfies the Schodinger equation and a normalization condition:

$$H_0\psi_0 = E_0\psi_0 \tag{4-89}$$

$$\int \psi_0^* \psi_0 dr^n = 1 \tag{4-90}$$

when the molecule is subjected to an external disturbing influence there is a contribution to the Hamiltonian H_1, due to the perturbation effect. The total Hamiltonian for the perturbed molcule is then,

$$H = H_0 + H_1 \tag{4-91}$$

Corresponding to this Hamiltonian there is a wave function and an energy E. The perturbed wave function can be written approximately as:

$$\psi = (1 + AH)\psi_0 \tag{4-92}$$

in which A is the variational parameter. This parameter is evaluated by requiring that the approximate value of the energy:

$$E = \int \frac{\psi H \psi dr^n}{\psi \psi dr^n} \tag{4-93}$$

be a minimum. Substitution of the Hamiltonian given in equation (4-91) and of ψ given equation in (4-93) into this expression for the energy gives,

$$E = \frac{\int \psi_0 (H_0 + H_1) + A(H_1 H_0 + H_0 H_1 + 2H_1^2 + A^2 (H_1 H_0 H_1 + H_1^3) \psi_0 \, dr^n}{\int \psi_0 (1 + 2AH_1 + A^2 H_1^2) \psi_0 \, dr^n} \qquad (4-94)$$

When use is made of the properties of the unperturbed wave functions, the expression assumes the form:

$$E - E_0 = \frac{W_1 + (Q_1 + 2W_2) A + (Q_2 + W_3) A^2}{1 + 2W_1 A + W_2 A^2} \qquad (4-95)$$

in which

$$W_1 = \int \psi_0 H_1 \psi_0 \, dr^n \qquad (4.96)$$

$$W_2 = \int \psi_0 H_1^2 \psi_0 \, dr^n \qquad (4-97)$$

$$W_3 = \int \psi_0 H_1^3 \psi_0 \, dr^n \qquad (4-98)$$

$$Q_1 = \int \psi_0 (H_0 - E_0) H_1 \psi_0 \, dr^n \qquad (4-99)$$

$$Q_2 = \int \psi_0 H_1 (H_0 - E_0) H_1 \psi_0 \, dr^n \qquad (4-100)$$

When the constant A is varied so as to minimize the value of E, equation (4-95) gives the shift in the energy level due to the perturbing effect. Let us now apply this result to the special case of a molecule in an electric field. In order to study the polarizability of a neutral molecule, the perturbation is taken to be uniform electric field of intensity E in the x direction. The perturbing potential is then

$$H_1 = - e E_x [- \sum_{i=1}^{n} x_i + \sum_{\alpha=1}^{\nu} Z_\alpha x_\alpha] \qquad (4-101)$$

Here e is the absolute value of the charge on an electron. The x_i and x_α are the x co-ordinates of the electrons and nuclei, respectively, and the Z_α are the atomic number of the nuclei. Now the x-component of the permanent dipole moment of the undistrubed molecule is given by

$$\mu_x = \int \psi_0 \left[- e \left\{ \sum_{i=1}^{n} x_i - \sum_{\alpha=1}^{\nu} Z_\alpha x_\alpha \right\} \right] \psi_0 \, dr^n$$

$$= - e \left[\sum_{i=1}^{n} \bar{x}_i - \sum_{\alpha=1}^{\nu} Z_\alpha x_\alpha \right] \qquad (4\text{-}102)$$

in which a bar indicates a quantum mechanical averaging with respect to the unperturbed wave function. Since all electrons are equivalent, we can drop the subscript on $\bar{x}_i$ and call is $\bar{x}$, the average x co-ordinate of an electron. Thus it may be seen that when the integral W_1 defined above is evaluated for the perturbation in equation (4-101), the result may be written as: $W_1 = -\mu_x E_x$. The expression given in equation (4-95) or the energy shift is then,

$$E - E_0 = \frac{-\mu_x E_x + A(Q_1 + 2W_2 - 2\mu_x^2 E_x^2) + A^2(Q_2 + W_3 + W_2 \mu_x E_x)}{1 - 2A\mu_x E_x + A^2 W_2} \qquad (4\text{-}103)$$

This expression for the energy shift is of the same form as equation $E - E_0$. Hence the evaluation of the integral Q_i and W_i enables us to calculate the co-efficient of E_x^2, which is simply related to the polarizability. First we notice from the definitions of the W_i that both the W_3 and $W_2 \mu_x E_x$ are proportional to E_x^3

Hence these terms do not contribute to the polarizability and need not be considered further here. The integral Q_1 may be shown to be zero, and the other integrals in equation (4-103) may be shown to have the following values:

$$W = \mu_x^2 \varepsilon_x^2 + e^2 \varepsilon_x^2 n \sqrt{\overline{(x - \bar{x})^2} + (n - 1)\, \overline{(x_1 - \bar{x})\,(x_2 - \bar{x})}} \quad (4\text{-}104)$$

$$Q = \tfrac{1}{2} a_0 e^4 n_x^2 \quad (4\text{-}105)$$

in which n is the number of the electrons in the molecule and $a_0 = \left(\frac{\hbar^2}{me^2} \right) = 0.5292$ Å is the Bohr radius. The term $\overline{(x_1 - \bar{x})^2}$ is the mean square deviation of an electron from its average position in the x direction. The term $\overline{(x_1 - \bar{x})}\ \overline{(x_1 - \bar{x})}$ gives the average correlation between the instantaneous x co-ordinates of two different electrons. This correlation would be zero for a molecular wave function. However, for polyatomic molecules this correlation is appreciably large if the wave function is either of a chemical bond using atomic orbitals or else the wave function is of the correlated molecular orbital type.

The variational parameter A may be determined by setting $\left(\frac{\partial E}{\partial A}\right)$ equal to zero and solving for A. In the limit of low electric field strength, it may easily be shown that A varies as E and the form,

$$A = \frac{\mu_x^2 \varepsilon_x^2 - W_2}{Q_2} \quad (4.106)$$

with the result that

$$E - E_0 = \mu_x \varepsilon_x - \frac{(\mu_x^2 \varepsilon_x^2 - W_2)^2}{Q_2} \quad (4\text{-}107)$$

Compariason of this result with equation (4-104) and the use of the expression given in equations (4-107), and (4-105) for Q_2 and W_2 yields the following formula for xx component of the polarizability.

$$\alpha_{xx} = -\frac{4n}{a_0} \left(\overline{(x_1 - \bar{x})} + (n-1)\, \overline{(x_1 - \bar{x})\,(x_2 - \bar{x})} \right)^2 \qquad (4\text{-}108)$$

This result, which is valid for molecules is a generalization of the expression for the polarizability of atoms which was obtained by Kirkwood (106).

The polarizability of an atom is isotropic. If the wave function for an atom is approximated by an atomic orbital wave function, the second term in equation (4-108) vanishes. Further more, in an atom $\bar{x} = 0$ and $\overline{x_1^2} = \overline{y_1^2} = \overline{z_1^2} = 1/3\ \overline{r_1^2}$. Thus equation (4-108) becomes,

$$\alpha = 4/9a_0 \sum_i n_i (\overline{r_i^2})^2 \qquad (4.109)$$

When n is the principle quantum number of an electron and $\overline{r_i^k}$ is given by the relation

$$\overline{r_i^k} = \frac{\int_0^\infty r^{k+2} |R_i|^2 dr}{\int_0^\infty r^2 |R_i|^2 dr} = \left(\frac{n_i^*}{2(Z - S_i)} \right)^k \left(\prod_{j=1}^{k} (2n_i^* + j) \right) a_0^k \qquad (4\text{-}110)$$

where n_i^* is the effective quantum number and $(Z - S_i)$ is the effective nuclear charge for various electrons in an atom.

Estimation of screening constants:

The polarizability can be estimated easily and quite accurately by means of "Screening constants" using the formulas (4-109) and (4-110). The basis for this treatment is the fact that an electron in an atom does not "feel" the presence of the nucleus completely, in as much as the electron is screened from nucleus by the other electrons. Hence, although the charge on the nucleus is Ze, and electron in the atom acts as though it is moving in the field of a nucleus of $(Z-S)e$. The quantity S is called the screening constant. From the knowledge of one property of an atom it is possible to determine a set of screening constants.

We assume that each electron in the atom may be represented by a wave function of the form,

$$\Psi_{n^*,l,m} = R_{n^*}(r)\, Y_l^m \quad (\phi,\theta)$$

$$R_{n^*}(r) = r^{n^*-1} \quad e^{-(Z-S)r/n^*} \qquad (4\text{-}111)$$

Hence the (Y_l^m) are the normalized spherical harmonics defined by the equation

$$Y_l^m(\theta,\phi) = i^{|m|-m}\sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}\; P_l^m(\cos\theta)\, e^{im\phi}$$

where is the units of the Bohr radius, $a_0 = 0.5292$ Å. At large distance this function behaves like a hydrogen like wave function of principle quantum number n in a field of nuclear charge $(Z-S)$. The effective quantum number n^* and the effective nuclear charge $(Z-S)$ for various electrons in an atom are given by the following empirical rules:

(i) If the principle quantum number of an electron is n the value of n^* is obtained from this table:

n	1	2	3	4	5	6
n^*	1	2	3	3.7	4	4.2

(ii) For determining (z-s), the electron are divided into the following groups, each having a different shielding constant:

1s	2s	3s	3d	4s	4d	5s	5d
	2p	3p		4p		5p	

That is the s and p for a given n are grouped together, but the d and the f each considered separately. The groups are considered to be arranged from inside out in the order given, above, with 1s as the inner most.

(iii) The screening constant S is found for any group of electrons from the following contributions.

(a) Nothing from any shell outside the one being considered.

(b) An amount 0.35 from each other electron in the group considered (except in the 1s group where 0.30 is used instead).

(c) If the shell considered is an s or p shell, an amount of 0.85 is contributed from each electron, with total quantum number less by one; and an amount 1.00 from each electron still further in.

(d) If the shell is a d or f shell each electron in the groups closer contributes 1.00 to the screening constant.

CHAPTER 5

CALCULATIONS AND RESULTS

5.1 Derivation of repulsive constants:

In order to take account different interactions existing in rutile structure (oxide crystals), the crystal energy can be expressed in equation (2-1) of chapter 2. When two ions combine to form a stable molecule two equilibrium conditions have been established. These are presented in chapter 1. At equilibrium position, the equilibrium distance r_o is called the bond length.

It may be observed that the bond between two atoms obey Hooke's law by taking the analogy of a spring. Thus the expression for restoring force may be written as:

$$F = - Ke\ (r - r_o) = - K_e x \qquad (5-1)$$

where K_e and r are the force constant and the inter nuclear distance respectively. Therefore the energy of a crystal is given by:

$$U(x) = U_{x=0} + K_e x^2 \qquad (5-2)$$

In this case, the energy curve is parabolic. The crystal formed by the analogy of Harmonic motion is called the simple harmonic oscillation and the frequency of the oscillation is given by

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{m}} \qquad (5-3)$$

where is the reduced mass of thesystem and the energy is given by

$$U_n = (n + \tfrac{1}{2})\hbar\sqrt{\frac{K}{m}} \qquad (5-4)$$

where n = 0,1,2 ...... etc.

For n = 0, equation (5-4) can be expressed as:

$$U_o = \tfrac{1}{2}\hbar\sqrt{\frac{K}{m}} = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\nu_e \qquad (5-5)$$

The expression (5-5) is called the zero point energy. The vibration of molecule results in only small distortion of the bond from its equilibrium length. If x is the displacement of the bond from its equilibrium length, a Maclaurin series expansion about x = o gives

$$U(x) = U_{x=0} + \left(\frac{dU}{dx}\right)_{x=0} + \tfrac{1}{2}\left(\frac{d^2U}{dx^2}\right)_{x=0} x + \ldots. \qquad (5-6)$$

At x = o, the potential energy is a minimum and therefore,

$$\left(\frac{dU}{dx}\right)_{x=0} = 0$$

If only the next higher term in the expansion is retained, the expression valids near the equilibrium position and have the form:

$$U(x) = U_{x=0} + \tfrac{1}{2}\left(\frac{d^2U}{dx^2}\right)_{x=0} x^2 \qquad (5-7)$$

Comparing this expression with equation (5-4) gives :

$$\left(\frac{d^2U}{dx^2}\right)_{x=0} = K_e \quad \text{or} \quad \left(\frac{d^2U}{dr^2}\right)_{r=r_o} = K_e$$

Thus the force constant is then the value of $\frac{d^2U}{dr^2}$ near equilibrium distance $r = r_o$

Now the total energy expression (5-1) of a crystal is again written as:

$$U = -\frac{\alpha_M Z^2 e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + \phi_r \qquad (5\text{-}8)$$

Here zero point is neglected because it has very small contribution to the total energy.

Now equation (5-8) can be also be written as

$$U = -\frac{\alpha_M Z^2 e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + \phi \qquad (5\text{-}9)$$

$$\frac{dU}{dr} = \frac{\alpha_M Z^2 e^2}{r^2} + \frac{6C}{r^7} + \frac{8D}{r^9} + \phi' \qquad (5\text{-}10)$$

$$\frac{d^2U}{dr^2} = -\frac{2\alpha_M Z^2 e^2}{r^3} - \frac{42C}{r^8} - \frac{72D}{r^{10}} + \phi'' \qquad (5\text{-}11)$$

From equation (5-10), we have,

$$r\frac{dU}{dr} = a + r\phi' \qquad (5\text{-}12)$$

where $a = \frac{\alpha_M Z^2 e^2}{r} + \frac{6C}{r^6} + \frac{8D}{r^8}$ (5-13)

and $r^2 \left(\frac{d^2U}{dr^2} \right) = b + r^2\phi$ (5-14)

where $b = -\frac{2\alpha_M Z^2 e^2}{r} - \frac{42C}{r^6} - \frac{72D}{r^8}$

but $r_o \left(\frac{dU}{dr}\right)_{r=r_o} = 3TV_m \beta / K$

and $r_o^2 \left(\frac{d^2U}{dr^2}\right)_{r=r_o} = \frac{9V_m}{K}$

Therefore (5-12) and (5-14) reduces to

$$a + r\phi' = \frac{3TVm\beta}{K} \qquad (5\text{-}15)$$

or $$r\phi' = \frac{3TVm\beta}{K} - a = M$$

$$\phi' = M/r \text{ where } M = \frac{3TVm\beta}{K} - a \qquad (5\text{-}16)$$

and $$b + r^2\phi'' = \frac{9Vm}{K} \qquad (5\text{-}17)$$

or $$r^2\phi'' = \frac{9Vm}{K} - b$$

or $$r^2\phi'' = \frac{9V_m}{K} - b = X$$

or $$\phi'' = \frac{X}{r^2} \text{ where } X = \frac{9V_m}{K} - b \qquad (5\text{-}18)$$

$$\frac{\phi''}{\phi'} = \frac{X}{r^2} \cdot \frac{r}{M} = \frac{X}{rM} \qquad (5\text{-}19)$$

After solving equation (5-19) the repulsive parameters can easily be found out for different repulsive potential.

A. BL potential (1918)

The form of the repulsive potential

$$\phi = A r^{-n} \qquad (5\text{-}20)$$

$$\phi' = n A r \qquad (5\text{-}21)$$

$$\phi'' = + n (n+1) A r \qquad (5\text{-}22)$$

$$\frac{\phi''}{\phi'} = - \frac{n(n+1) Ar^{-(n+2)}}{n Ar^{-(n+1)}} = \frac{X}{rM} \qquad (5\text{-}23)$$

or $$\frac{n+1}{r} = - \frac{X}{rM} \text{ or, } n+1 = - \frac{X}{M}$$

$$n = - \left(\frac{X}{M} + 1\right) = - \frac{X}{M} - 1 \qquad (5\text{-}24)$$

From equation (5-15) one can write

$$a + r\,\phi' = \frac{3TV_m\beta}{K}$$

$$r\,\phi' = \frac{3TV_m\beta}{K} - a = M \qquad (5\text{-}25)$$

Substituting (5-21) in equation (5-25) it may easily write that,

$$r\,(-\,n\,A\,r^{-(n+1)}) = M$$

$$A = -\frac{M}{nr}\,r^{(n+1)} = -\frac{M}{n}\,r^{n}$$

$$= -\frac{M}{n}\,r^{n} \qquad (5\text{-}26)$$

B. BM potential:

The form of repulsive potential as:

$$\phi = B\,e^{-r/\rho} \qquad (5\text{-}27)$$

$$\phi' = -\frac{B}{\rho}\,e^{-r/\rho} \qquad (5\text{-}28)$$

$$\phi'' = \frac{B}{\rho^2}\,e^{-r/\rho} \qquad (5\text{-}29)$$

substituting equation (5-28) and (5-29) in (5-19) one can obtain,

$$-\frac{\frac{B}{\rho^2}\,e^{-r/\rho}}{\frac{B}{\rho}\,e^{-r/\rho}} = \frac{X}{rM}$$

$$\text{or} \quad 1/ \quad = -\frac{X}{rM}$$

$$= -\frac{Mr}{X} = -\frac{M}{X}\,r \qquad (5\text{-}30)$$

From equation (5-15) may easily write that

$$a + r\,\left(-\frac{B}{\rho}\,e^{-r/\rho}\right) = \frac{3TV_m\beta}{K}$$

$$\text{or, } r\,\frac{B}{\rho}\,e^{-r/\rho} = -M$$

$$\text{or, } B = -\frac{M}{r}\rho\,e^{-r/\rho}$$

$$B = -\frac{M}{r}\rho\,e^{+r/\rho} \qquad (5\text{-}31)$$

C. Verwey potential:

The form of the repulsive potential as:

$$\phi = \mu\, r^{-12} \qquad (5\text{-}32)$$

$$\phi' = -12\mu\, r^{-13} \qquad (5\text{-}33)$$

$$\phi'' = -13 \times 12\mu\, r^{-14} \qquad (5\text{-}34)$$

Substituting equations (5-33), (5-34) in (5-19) it can be written as:

$$-\frac{156\mu r^{-14}}{12\mu r^{-13}} = \frac{X}{rM}$$

$$\text{or } 13\, r^{-1} = -\frac{X}{rM}$$

$$\text{or } 12 = -\frac{X}{M} - 1 \qquad (5\text{-}35)$$

From equation (5-15) one may write,

$$a + r\,(-12\mu\, r^{-13}) = \frac{3TV_m\beta}{K}$$

$$\text{or, } r(-12\mu\, r^{-13}) = M$$

$$\text{or, } 12\mu\, r^{-12} = -M$$

$$\text{or, } \mu = -\frac{M}{12}\, r^{12} \qquad (5\text{-}36)$$

D. VS potential:

The form of the repulsive potential as:

$$\phi = \lambda_1 e^{-K_1 r^2} \qquad (5\text{-}37)$$

$$\phi' = -\lambda_1 K_1 \, 2re^{-K_1 r^2} \qquad (5\text{-}38)$$

$$\phi'' = -2\lambda_1 K_1 \, e^{-K_1 r^2} + 4r\lambda_1 K_1^2 \, e^{-K_1 r^2} \qquad (5\text{-}39)$$

Substituting equation (5-38) and (5-39) in equation (5-19) one may obtain:

$$K_1 = -\left(\frac{X}{M} - 1 \right)/2r^2 \qquad (5\text{-}40)$$

From equation (5-15) it can be written as:

$$r(-\lambda_1 K_1 \, 2re^{-K_1 r^2}) = M$$

or, $$\lambda_1 = -\frac{M}{2r^2 K_1} e^{K_1 r^2} \qquad (5\text{-}41)$$

E. GT potential:

The form of the repulsive potential as:

$$\phi = \frac{p}{r} e^{-Kr^2} \qquad (5\text{-}42)$$

$$\phi' = -\frac{pK}{r} \, 2r.e^{-Kr^2} - \frac{pe^{-Kr^2}}{r^2}$$

$$= -2\frac{pK}{\ } e^{-Kr^2} - \frac{pe^{-Kr^2}}{r^2}$$

$$= -2pk \, e^{-Kr^2} \frac{pe^{-Kr^2}}{r^2} \qquad (5\text{-}43)$$

$$= - \frac{(2\, Kr^2 + 1)}{r^2}\, p\, e^{-Kr^2} \qquad (5\text{-}44)$$

$$\phi'' = - 2pk. - K.2r.\, e^{-Kr^2} + \frac{p.K.2r\, e^{-Kr^2}}{r^2} + \frac{2p\, e^{-Kr^2}}{r^3}$$

$$= 2pe^{-Kr^2}\left(2\, k^2\, r + \frac{K}{r} . \frac{1}{r^3}\right)$$

$$= 2pe^{-Kr^2}\left(\frac{2K^2r^4 + Kr^2 + 1}{r^3}\right) \qquad (5\text{-}45)$$

Substituting equations (5-44) and (5-45) in (5-19) one may write as:

$$\frac{2\,pe^{-Kr^2}\left(\dfrac{2\,K^2r^4 + Kr^2 + 1}{r^3}\right)}{-pe^{-Kr^2}\,(2Kr^2 + 1\ /r^2)} = \frac{X}{rM}$$

$$\text{or,}\quad \frac{2K^2r^4 + Kr^2 + 1}{r^3} \times \frac{r^2}{2Kr^2 + 1} = - \frac{X}{2rM}$$

$$\text{or,}\quad \frac{2K^2r^4 + Kr^2 + 1}{2Kr^2 + 1} = - \frac{X}{2M} \qquad (5\text{-}46)$$

Let $- \frac{X}{2M} = a$.

Then equation (5-46) becomes,

$$\frac{2K^2r^4 + Kr^2 + 1}{2\,Kr^2 + 1} = a$$

Therefore, $2\, k^2 r^4 + kr^2 + 1 = 2kr^2 + a$

or, $2\, r^4 k^2 + r^2 k + 1 - 2\, r^2 ka - a = 0$

or, $2r^4 k^2 + r^2 (1-2a) K + (1-a) = 0$ (5-47)

This is the quadratic equation in K.

Therefore the solution of equation (5-47) is

$$K = \frac{-1 + 2a \pm - 7 + 4a + 4a^2}{4r^2} \qquad (5\text{-}48)$$

From equation (5-15) one may obtain,

$$P = \frac{Mre^{Kr^2}}{(2Kr^2 + 1)} \qquad (5\text{-}49)$$

F. Islam potential:

The form of the potential is

$$\phi = I\, e^{-\lambda r^{\sigma}} \qquad (5\text{-}50)$$

Let $m = \lambda r^{\sigma}$, $\sigma = Z + \frac{1}{Z} \frac{\Delta r}{r_o}$

$$\phi = I\, e^{-m} \qquad (5\text{-}51)$$

$$\phi' = - \sigma \frac{m}{r} \phi \qquad (5\text{-}52)$$

$$\phi'' = - \sigma \frac{m}{r} \phi' - \sigma(\sigma - 1) \frac{m}{r^2} \phi \qquad (5\text{-}53$$

$$\frac{\sigma \frac{m}{r} \phi' - \sigma(\sigma - 1)\, m/r^2\, \phi}{- \sigma m/r\, \phi} = \frac{X}{rM}$$

$$\frac{-\sigma m/r . - \sigma m/r . \phi - \sigma(\sigma - 1) m/r^2 \phi}{-\sigma m/r\, \phi} = \frac{X}{rM}$$

or, $$\frac{\sigma^2 m^2/r^2 \phi - \sigma(\sigma - 1) \frac{m}{r^2} \phi}{-\sigma m/r\, \phi} = \frac{X}{rM}$$

or, $$\frac{\sigma m/r^2 \phi\, (\sigma m/r - (\sigma - 1)/r\,))}{\sigma m/r\, \phi} = \frac{X}{rM}$$

or, $$\frac{\sigma m}{r} - \frac{(\sigma - 1)}{r} = - \frac{X}{rM}$$

or, $(\sigma m - \sigma + 1) = - x/M$

or, $\alpha(m - 1) + 1 = - x/M$

or, $\alpha(m - 1) = - \frac{X}{M} - 1 = - \left(\frac{X}{M} + 1 \right)$

or, $m - 1 = - \frac{1}{\alpha} \left(\frac{X}{M} + 1 \right)$

or, $m = - \frac{1}{\alpha} \left(\frac{X}{M} + 1 \right) + 1$ (5-54)

But $m = \lambda r^{\alpha}$

$\therefore \quad \lambda = \frac{m}{r^{\alpha}}$ (5-55)

Now from equation (5-15) one may obtain,

$$a + r \left(-\alpha \frac{m}{r} \phi \right) = \frac{3\pi V_m \beta}{K}$$

$$a - m\alpha I \, e^{-m} = \frac{3\pi V_m \beta}{K}$$

$$I m \alpha \, e^{-m} = a - \frac{3\pi V_m \beta}{K} = - M$$

$$I = - \frac{M}{m\alpha} e^{m} = - \frac{M}{m\alpha} e^{m} \tag{5-56}$$

G. Proposed new potential:

The form of the potential is

$$\phi(r) = \frac{G}{r^{n}} e^{-gr^{\alpha}} \tag{5-57}$$

Where $\alpha = Z + \frac{1}{Z} \frac{\Delta r}{r_o}$, $n = 3$

Let $m = gr^{\alpha}$

$$\phi' = - (3 + \alpha m) \frac{\phi}{r} \tag{5-58}$$

$$\phi'' = (12 + 3\alpha m - \alpha(\alpha - 4)m + \alpha^2 m^2)\frac{\phi}{r^2} \qquad (5\text{-}59)$$

and

$$\phi = (-60 + 12\alpha m + 3\alpha(\alpha - 5)m - 3\alpha^2 m^2 - \alpha(\alpha-4)(\alpha - 5)m + \alpha^3(\alpha - 4)m^2 + \alpha^2(2\alpha-5)m^2 - \alpha^3 m^3)\frac{\phi}{r^3} \qquad (5\text{-}60)$$

By solving equation (5-57) and equation (5-58) one obtains.

$$m = \frac{(\alpha^2-7+\alpha a)+(\alpha^2-7+\alpha a)^2-4\alpha^2 3(4-a)}{2\alpha^2} \qquad (5\text{-}61)$$

and from equation (5-57) it can be easily written that

$$G = -\frac{M r^3 e^m}{(3+\alpha m)} \qquad (5\text{-}62)$$

H. Buckingham potential:

The form of the potential is

$$\phi(r) = A e^{-r/\rho} - C/r^6 \qquad (5\text{-}63)$$

James and Catlow[159] has given the following values for the parameters appropriate for the nearest neighbour and next nearest neighbour interactions

For TiO_2:

$A_{+-} = 656.7$ ev, $_{+-} = 0.40431$ Å, $C_{+-} = 0$

$A_{--} = 22764.3$ ev, $_{--} = 0.1490$ Å, $C_{--} = 27.063$ ev Å^{-6}

For SnO_2:

$$A_{+-}=1056.8 \text{ ev}, \ \rho_{+-} = 0.3683 \text{Å}, \ C_{+-}=0$$

$$A_{--}=22764.3 \text{ ev}, \ \rho_{--} = 0.1490 \text{ Å}, \ C_{--}=28.43 \text{ ev Å}^6$$

5.2 Electronic polarizability and van der Waals constants:

a) Electronic polarizability:

The electronic polarizability plays a very important role in several of the theories of long range intermolecular forces. Matter is made up of two kinds of charges, free and bound. Free charges can move through considerable distances, whereas bound charges such as the electrons in atoms can shift their average positions only by distances small compared to atomic dimensions, that is, by a small fraction of an angstrom. An electron in an atom maintains a stationary orbit by balancing the force of attraction towards the nucleus with centrifugal force generated by its motion. The internal electronic forces in atoms and molecules are very large compared to the forces produced by external electric fields. In a conductor a fraction of the electrons are free to move from one place to another. These free electrons distribute themselves so as to make the electric potential constant throughout the conductor. Any other distribution of free electron would have a higher energy. In an insulator the electrons are firmly attached to individual atoms, molecules or ions. When such a insulator is placed in an electric field, the electrons are pulled slightly in one direction while the nuclei are pulled in the oposite direction. This relative displacement of charges in matter is referred to as polarization. When two molecules approach one another a mutual polarization takes place. This polarization of the molecules may be an important contribution to the intermolecular potential. The extent to which the polarization takes place can be obtained from a study of the electric susceptiblity of the bulk substances. The detailed study of polarizability are discussed in chapter 4.3 of this thesis.

According to Pauling the free state polarizability α_i of an atom or ion can be expressed in an approximate manner as follows:

$$\alpha_i = KZ \qquad (5\text{-}64)$$

Where Z is the nuclear charge and k is a constant depending upon structure of the ion. Because ions and atoms of the same species have different electrical environments, the polarizability of an ion or atom varies some what with the substances. Thus a different set of polarizability obtained for different ion environment. The α - values of Si^{4+} Ti^{4+}, Sn^{4+} and O^{2-} are available in literature are shown in Table -1. TKS values are shown in column 4 of Table -1. The free ion polarizability values are presented in column 2 of Table-1. It can be observed from Table -1 that polarizability values for some ions in a particular column or set are missing. Thus we estimated a consistant set of a α-values for all the ions under discusion by means of " Screening Constant " method and are shown in Table-1. The basis of this treatment is the fact that an electron in an ion does not " feel" the presence of the nucleus completely, in as much as the electron is screened from the nucleus by the other electrons.

Table - 1 : Electronic Polarizability of ions (in Å^3).

Ion	Pauling[a]	FJ[b]	TKS[c]	Present study Set I	Set II	Effective numbers of electron
Si^{4+}	0.017	0.04	-	0.05	0.04	14
Ti^{4+}	0.185	0.24	-	0.63	0.24	19
Ge^{4+}	-	-	1.0	0.80	1.0	21
Sn^{4+}	-	-	3.4	3.64	3.4	29
O^{2-}	3.88	2.75	0.5 to 3.2	2.16	2.75	7

Set II : Reference No. b with missing values from reference No. c.

a. Ref. 131

b. Ref. 127

c. Ref. 132

(b) van der Waals constants.

The van der Waals constants C and D are the linear combinations of the van der Waals coeffients (c_{ij},d_{ij}) for interactions of the various ions pairs weighted by appropriate lattice sums. The detailed study for van der Waals energy, co-efficients are presented in chapter iv. Here the above studies are described very shortly. In this thesis SK treatment based on variational theory is used mainly for deriving (c_{ij},d_{ij}). This treatment is most appropriate than others. Because in London and KM formulas have large uncertainties. Thus one expresses the van der Waals energy as in eqn.(4-4). Where the constants have their usual meaning. The calculated value of van der Waals constants are shown in Table 2.

5.3 Lattice sums.

The lattice sums for rutile type compounds are obtained by summing l_{ij}/r_{ij}^6(for S) and l_{ij}/r_{ij}^8 (for T),where l_{ij} is the number of j ions distant r_{ij} from ion i.The lattice sums for rutile type compounds studied are listed in Table 2.

5.4 Effective number of electrons:

The effective number of electrons are the number of outermost electrons of the cation and the anion. The values of c_{ij} when fitted in eqn. given below $c_{ij} = 3/2 . e\hbar/m^{1/2} . \alpha_i \alpha_j/(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}$ give the effective numbers of electrons Ni or Nj which show a smooth trend of variation with atomic number Z . It has been suggested →

→ by Scott and Scherage [12] that the plot of N_{eff} vs Z_{eff} (Fig.5-1) can be used to predict the values of N for any atom or ion. Values of N_j and N_i for rutile so obtained are given in Table-1.

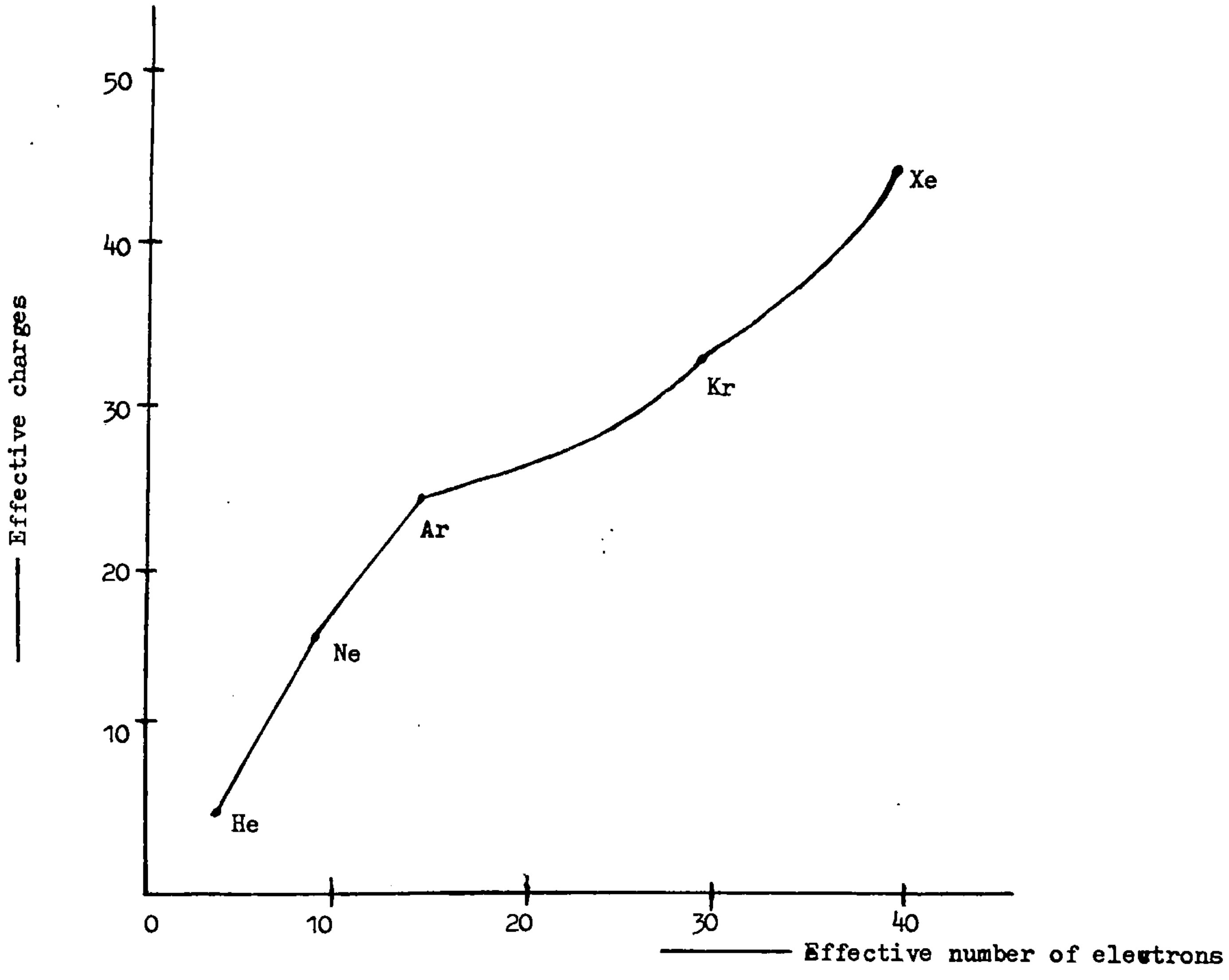


Fig. 5-1 : Plot of effecyive number of electrons versus effective charges.

Table - 2 : Input data

Crystal	r_o (Å)	K*** (10^{-13} cm^2/dy.)	C (10^{-60} erg-cm^6)	D (10^{-76} erg-cm^8)	Ionic radii (Å)**		Madelung constant (Rutile type	
					r+	r-		
SiO_2	1.757	2.78	172.80 234.53	77.64 116.03	0.506	1.251	4.77	2.212
TiO_2	1.945	4.91	443.08 354.24	236.92 198.23	0.94	1.005	4.77	2.22
GeO_2	1.872	3.86	523.91 743.87	283.40 453.51	0.59	1.282	4.77	2.185
SnO_2	2.052	4.69	1729.66 1941.75	1045.41 1283.69	0.79	1.261	4.77	2.115

Different entries for C and D corresponding for different sets of polarizability values.

** Ref. 128

*** Ref. 129

Contd.....

Contd --- Table - 2 : Input data

Crystal	Lattice sums* of four oxides						$-U_{SR}^{vdW}$ (Kcal/mol)
6	S_{+-}	S_{++}	S_{--}	T_{+-}	T_{++}	T_{--}	
SiO_2	5.963	0.362	1.382	5.646	0.128	0.671	96.90 133.20
TiO_2	6.097	0.371	1.412	5.794	0.131	0.688	134.51 108.16
GeO_2	6.165	0.375	1.425	5.841	0.132	0.694	202.36 291.20
NsO_2	6.383	0.339	1.487	6.131	0.139	0.729	331.52 433.34

* Ref. 127

5.5 Repulsive parameters and energy:

The repulsive parameters and energies calculated under study, have been shown in table 3 and in table 4. Different repulsive forms have been used for calculating the parameters and energies.

Table - 3 : Values of repulsive parameters.

Crystal	Polarizability set	B - L		B - M		Verwey	V - S	
		n	$ar^{-n}(10^{-12}$ erg)	$(10^{-8}$ cm)	$B(10^{-12}$ erg)	$r^{-12}(10^{-12}$ erg)	$_1(10^{-12}$ cm)	$_1e^{-K_1r^2}(10^{-12}$ erg)
SiO_2	I	4.34	67.42	1142.96	329	24.38	1098.96	46.15
	II	4.45	69.37	1315.96	322	25.72	1202.66	47.86
TiO_2	I	4.12	68.69	928.96	380	23.61	988.66	46.25
	II	4.04	67.41	829.91	386	22.66	920.98	45.06
GeO_2	I	4.45	72.61	1381.70	343	26.93	1260.95	50.10
	II	4.67	77.71	1856.75	330	30.24	1527.84	54.41
SnO_2	I	5.13	74.18	2836.29	335	31.68	1880.46	53.35
	II	5.21	77.47	3217.94	331	33.60	2053.32	55.97

Contd.......

Contd... Table - 3 : Values of repulsive parameters

Crystal	G - T			Islam		Buckingham		M. Islam	
	$P(10^{-20}$	$K_2(10^{16}$	$P/r^2\ e^{-K_2r}$ $(10^{-12}\ erg)$	$I(10^{-22}\ erg)$	$mc = r^-$	$\phi(r) = Ae^{-r/}$	$-C/r^6(10^{-12}\ erg$	$mc_1 = gr^-$	G
SiO_2	1046.49	0.80	48.71	866.71	2.96		-	1.04	847.14
	1146.58	0.83	50.41	940.85	3.01		-	1.10	927.26
TiO_2	1039.74	0.63	49.03	777.99	2.86		8.25	0.91	1030.62
	967.60	0.62	47.86	727.58	2.82		-	0.85	959.58
GeO_2	1280.88	0.73	52.77	1015.47	3.04		-	1.11	1187.04
	1555.58	0.76	58.00	1220.17	3.14		-	1.24	1439.49
SnO_2	2108.38	0.69	55.64	1610.95	3.42		6.26	1.52	2420.52
	2303.98	0.70	58.31	1755.52	3.46		-	1.57	2645.84

Table - 4 Different types of repulsive energies.

Crystal	Polarizability set	Calculated repulsive energy in Kcal/mol							
		B- L	B - M	Verwey	V - S	G - T	Islam	Buckingham	M. Islam
SiO_2	I	970.80	789.02	351.14	664.57	701.40	643.07	-	794.96
	II	998.97	815.61	370.30	689.12	725.90	667.19	-	816.77
TiO_2	I	989.26	796.20	339.98	666.19	706.10	643.08	118.97	813.28
	II	970.66	777.86	326.35	648.96	689.55	626.14	-	800.27
GeO_2	I	1045.64	853.82	387.86	721.47	759.93	701.37	-	857.37
	II	1118.95	921.62	435.48	783.45	822.24	762.31	-	915.77
SnO_2	I	1068.14	893.74	456.15	768.30	801.22	756.14	90.19	880.10
	II	1115.61	935.81	483.89	805.93	839.63	793.32	-	919.51

5.6 Output results:

5.6.1 Lattice energy:

The lattice energies for rutile-type oxide crystals have been calculated using the expression (5-9) of this chapter.

The results of the calculations using two different sets of electronic polarizability as well as seven different forms (A-G) for the repulsive interactions are presented in Table 5 This 5 also contains experimental values of the lattice energy for comparison.

5.6.2 Pressure derivative of Bulk moduli:

The potential represented by (5-9) has also been used to calculate the pressure derivative of Bulk moduli, $\frac{dB}{dp}$. The results of the calculations obtained for $\frac{dB}{dp}$ are listed in Table 6 with available experimental values for comparison.

Table - 5 : Lattice energies of four Rutile-type oxides. (SiO_2, TiO_2, GeO_2, SnO_2)

Crystal	Polarizability set	- U (Kcal/mol.) Calculated								-U(Kcal/mol) Experimental
		B - L	B - M	Verwey	V - S	G - T	Islam	Buckingham	M. Islam	
SiO_2	I	2733.73	2915.51	3353.39	3039.95	3003.22	3061.45	-	2909.56	3166[a]
	II	2741.85	2925.21	3370.52	3051.70	3014.92	3073.63	-	2924.65	
TiO_2	I	2404.16	2579.22	3053.44	2727.24	2697.33	2750.34	3139.89	2580.14	2858[a],2873[c]
	II	2396.41	2589.21	3040.72	2718.11	2677.92	2740.94	-	2566.81	2900[d],2930[e]
GeO_2	I	2542.72	2734.54	3200.50	2866.89	2828.43	2886.99	-	2730.99	3037[a],3050[d]
	II	2559.25	2756.58	3242.72	2894.75	2855.96	2915.87	-	2762.43	3090[e]
SnO_2	I	2402.36	2576.76	3014.34	2702.20	2669.28	2714.35	2998.88	2590.34	2783[a],2924[d]
	II	2406.7	2586.51	3038.44	2716.39	2682.69	2729.00	-	2602.80	2838[e]

a Ref. 127
c Ref. 129
d Ref. 130
e Ref. 131

Table - 6 : Pressure Derivative of Bulk Modulus

Crystal	Polarizability set	dB/dp								Experimental dB/dp
		B - L	B - M	Verwey	V - S	G - T	Islam	Buckingham	M. Islam	
SiO_2	I	3.57	2.88	6.47	1.52	1.51	1.70	-	3.07	7.00[f]
	II	3.54	2.79	6.52	1.43	1.44	1.53	-	2.97	-
TiO_2	I	3.30	2.46	6.54	1.14	1.28	0.98	-	2.76	6.76[g]
	II	3.33	2.54	6.51	1.22	1.33	1.14	1.56	2.86	-
SnO_2	I	3.33	2.42	6.62	1.09	1.23	0.91	-	2.64	6.16[g]
	II	3.24	2.18	6.71	0.88	1.09	0.44	-	2.36	-
SnO_2	I	3.49	2.36	6.83	0.93	1.11	0.66	-	2.44	5.13[g]
	II	3.46	2.24	6.88	0.83	1.06	0.43	1.30	2.30	-

f Ref. 132

g Ref. 133

CHAPTER 6

DISCUSSIONS AND CONCLUSIONS

Wackman et.al.[129] discussed the effect of polarizabilities on energy values for TiO_2 beacuse these are not known exactly. They found that binding energy changes by more than 10%. When one set of values is replaced by those obtained by Ruffa's method[134]. In view of this extreme situation with Ruffa's polarizability values Wackman et.al.[129] considered that these values of ions are incorrect. Thus the part played by polarizability is apparent. The values of Si^{4+}, Ti^{4+}, Sn^{4+} and O^{2-} available in the literature [111,115,116,129]are shown in Table 1. TKS values [116] of simple additivity in oxide crystal leads to an appreciable spread of the values of polarizability. As suggested by TKS [116] this would result from a departure from the ideal ionic crystal state and an overlapping and distortion of the ionic wave function. TKS [116] values give an approximate measure of various ions in crystals rather than of "free" ions. On the other hand, the polarizability values in column 2 are those for free ions. The experimental work suggests a significant dependence of the values on the environment. The crystalline environment significantly reduces the polarizability of the anions and increase the polarizability values of the cations.

The value for $\alpha(Si^{4+})$ derived by us is consistent with the value of 0.04 X 10 nm^3 obtained by Born and Heisenberg[137], an analysis of the Rydberg Ritz correction for a spectral series. From the indices of refraction of salts in aquous solution, Fajan and Joos [127] also obtained the same value but Schmidt et.al. [154] reported its value to be 0.51 X 10 nm^3 and 0.66 X 10 nm^3 The first one refers to the result when the influence of both the environment in the crystal and self consistency is not included. In their study the effect of the crystal environment is incorporated by the Watson-sphere model, while consistency effects are included by a procedure adopted from many body perturbation theory. The polarizability values of both Ge^{4+} and Sn^{4+} are found to be consistent with the TKS values $\alpha(O^{2-})$ is consistent with the crystal have values by Bisarya and Shanker [155].

Table 1 shows different sets of polarizability values, including free ion sets and the choice of values is not necessarily clear-cut. It was thus thought to be of interest to see how sensitive the results were to the specific choice of polarizability and so a range of polarizability values with reasonable physical justification will be considered. The use of different sets of values affects constants and hence other calculations. There is no direct method which can yield experimental values of vdW energy in ionic crystal. It has been indicated by many authors that the London formulae involved excitation energies of ions which are subject to large uncertainties and these seriously under estimate the actual vdW interations. Thus the vdW Co-efficients c_{ij} and d_{ij} are estimated using SKV approach to obtain an increased vdW bonding effect.

The estimated values (set I) are used to calculate the values of C and D based on variational method. The values of vdw energies calculated by Ladd [127] and by Shaker and Jain [128] vary between 40 to 50 and 50≈ 100 Kcal/mol., respectively for the compounds under discussion. The results are much smaller than those obtained from present calculations.

The repulsive energy contributions to the total energy for various crystals have been shown in the six columns of Table 4. Eight short-range repulsive interactions are considered. It is observed that the repulsive potential energy increases with the increase of vdW energy. The contribution of the second neighbour repulsion is small. For this reason we have not included the contribution of the second neighbour interaction in the repulsive energy calculations, except for one case as mentioned earlier.

As shown in table 5 for any particular repulsive potential form the values of the lattice energies are seen to vary from one set of polarizability values to another. However the variation is small. For a particular set of polarizability values, the lattice energy vary appriciably when different repulsive potentials are used. The lattice energy using Born-Lande form with set I polarizability is lower than on the average experimental values by 14.86%, but in case of Born-Mayer, Islam, Modified Islam and Buckingham potential forms the discrepancy is 3.50%-9%. In the case of Verwey, Varshni-Shukla, Gohel-Trivedi forms the corresponding values differ from experimental values by amount of -6.60% 4.25%, and 5.52% respectively.

In the light of the above calculated results it is seen that although the calculated values are not in exact agreement with the experimental values the deviations or discrepancies are not much except Verwey and Buckingham potential. This situation reveals that the ionic character of these crystals are nearly correct.

Earlier investigations [73,129] assumed the short-range parameters to be equal i,e. $\rho_{+-}=\rho_{--}=\rho$. In an attempt to remedy this deficiency Shanker and Jain [128] used a more general short-range repulsive interaction but could not determine ρ_{+-} because of the lack of ρ_{i-} values for tetravalent positive ions. They chose ρ_{+-} =0.0345 nm^3 for all oxide crystals. This model which assumes a full ionic charge including a vdW energy term. and the resulting dB/dp values were found to be not very satisfactory.

Anderson and Anderson [132] within the framework of a simple Born model also calculated dB/dp for SiO_2 and TiO_2 by adjusting the potential parameters until they yield the correct value of bulk modulus. Shanker and Jain [144] pointed out that these results clearly demonstrated the fact that even the fitting of the bulk modulus did not improved the agreement between theory and experiment. Contrary to this agreement our simple approach showed that not only lattice energy values but also dB/dp values yield much agreement with experiments than those due to either Shanker and Jain [128] or Anderson and Anderson [132].

Anderson and Anderson [132] suggested that the directional and bond-bending forces are most likely present in these crystals. Striefler and Barsch [141] used the rigid ion model of Katiyar [84] where central force short-range interaction between first and second nearest neighbours is included and an effective charge takes into account deviations from ionic binding. The six free parameters were determined from a least-square fit of the Raman and inactive frequencies and of the elastic constants to the available experimental data. They concluded that the application of the model to the rutile-type oxides turned out to be much less satisfactory than for fluorides [141]. They than added harmonic angle bending forces for the five O pairs showing a common, nearest neighbour cation and a least squares technique fitted the nine free parameters. Their results for dB/dp are much better than all previous calculations, but as pointed out by Shanker and Jain [144] this improvements of dB/dp has been achieved at cost of reducing the ionic charges which are about one third of the nominal values, such small ionic charges would reduce the Madelung energy and hence the lattice energy significantly with respect to the experimental energy.

With the same polarizability values the potential with the B-M repulsion reduces the lattice energies to within 8.59% of the experimental values, where as this is not so for dB/dp. In the case of B-M repulsion, the pressure derivative of bulk modulus dB/dp shows a derivative from average experimental values amounting to 59% . But the use of the modified islam potential the lattice energy agrees within 8.7% compared to the experimental values and the dB/dp is on the average 56% smaller compared to the experimental value. Although with B-L form, the lattice energy, dB/dp show a deviation from experimental value by 14.86% and 44.55% respectively. Hence it may be remarked that the present approach with the new modified Islam potential seem~~s~~ to be able to describe resonably both the lattice energy and dB/dp values simultanuously. The improvement results mainly from the inclusion of vdW energy calculated with a estimated consistent set of polarizability values obtained in the study and the new modified Islam potential. The resulting values seems to imply that the binding in rutile, while somewhat more ionic than some of the previous studies would indicate, (e.g. Baur, [130] and Kingsbury) [142] whose calculation suggested an appreciable covalent character in the M-O bond because the calculated lattice energies have been found to 25% larger or more positive than the thermodynamic values) does contain a covalent contribution.

It is worth mentioning here that theoretical models based on rigid ion and shell models, with either axially symmetric or tensor the first and second neighbour forces have been fitted to the measured dispersion relation available fully for TiO only [150]. It was also shown that both the second neighbour rigid-ion and shell models, when used with central forces are unable to predict the qualitative features and only the shell model with tensor forces for all interaction except the second neighbour O-O interaction was able to give acceptable qualitative agreement with data and that agreement is good for only some models. From this discussion it is apparent that a comprehensive theory which can correlate all physical properties of rutile-type compounds, is still not available. In view of this we conclude that a relatively simple treatment with a newly derived polarizability set is moderately successful in explaining at least some of the properties of the compounds under study.

```
C     CALCULATION OF LATTICE ENERGIES AND PRESSURE DERIVATIVE OF BUL
C.    MODULI.
      PROGRAM   CLLE
      IMPLICIT  REAL(A-Z)
      INTEGER   MAXROW,MAXCOL,IROW,JCOL
      CHARACTER NULL
      CHARACTER COMP*4
      PARAMETER (MAXROW=00004,MAXCOL=00024,NN=7.0)
*
      DIMENSION DI1 (MAXROW,MAXCOL)
      DIMENSION DI2 (MAXROW,MAXCOL)
      DIMENSION DI1(8,15),DI2(8,23)
*
      OPEN(UNIT=22,STATUS="OLD",FILE="CLLE.DAT")
      OPEN(UNIT=11,STATUS="NEW",FILE="CLLE.OUT")
      OPEN(UNIT=33,STATUS="NEW",FILE="CLLE.TXT")
C     --Calculation of van der Waals co-efficients (D.D)--
      READ (22,998) NULL
      READ (22,998) NULL
*
      DO 10000 IROW=1,4
      READ (22,100) COMP,AP,AN,NP,SPN,SPP,SNN,TPP,TNN,TPN,R,VM,BT,K,
C     IF(AP .EQ.100.0)GOTO 111
      I=I+1
C     ----------------------------
      A1=AP*AP*.5
      A2=(AP/NP)**.5
      A3=A1/A2
      CPP=A3*25.20
C     WRITE(11,*)CPP
C     ---------------
      B1=AN*AN*.5
      B2=(AN/NN)**.5
      B3=B1/B2
      CNN=B3*25.20
C     WRITE(11,*)CNN
C     -------------
      C1=AP*AN
      C2=(AP/NP)**.5+(AN/NN)**.5
      C3=C1/C2
      CPN=C3*25.20
      WRITE(11,*)"CPN =",CPN,"CNN =",CNN,"CPP =",CPP
C     -------------------
      CV=CPN*SPN+CPP*SPP+CNN*SNN
C     WRITE(11,*)"CV = ",CV
C     calculation of van der Waals co_efficients(D.Q)
C
      FR=6.666
      D1=AP*AN
      D21=(AP/NP)**.5
      D22=(AN/NN)**.5
      D2=(D21+D22)**2
      D31=(AP/NP)
      D32=SQRT((AP*AN)/(NP*NN))*6.66
      D33=(AN/NN)
      D3=D31+D32+D33
      D4=D1*D2/D3
      DPN=D4*41.34
C     WRITE(11,*)"DPN = ",DPN
C     ---------------
      E1=AP*AP
      E2=(2*(AP/NP)**.5)**2
      E3=2*(AP/NP)+FR*(AP/NP)
      E4=E1*E2/E3
      DPP=E4*41.34
C     WRITE(11,*)DPP
```

```
      F1=AN*AN
      F2=(2*(AN/NN)**.5)**2
      F3=2*(AN/NN)+FR*(AN/NN)
      F4=F1*F2/F3
      DNN=F4*41.34
      WRITE(11,*)DNN
C     DV =DPN*TPN+DPP*TPP+DNN*TNN
      WRITE(11,*)"DV= ",DV ,"DPN= ",DPN, "DPP =",DPP ,"DNN =",DNN
      T      =14.40
C     calculation of van der Waals energies
      UDD=(-CV/(R**6))*T
      UDQ=(-DV/(R**8))*T
      UVT=UDD+UDQ
      WRITE(11,*)"UVT=",UVT
      WRITE(11,*)"UDD=",UDD
      WRITE(11,*)"UDQ=",UDQ
C     Calculation of Repulsive Energies.
      TP=300.0
C     ------------BL-----------
      A=(440.18/R)+(6*CV/R**6)+(8*DV/R**8)
      B=-(880.36/R)-(42.*CV/R**6)-(72*DV/R**8)
      M=1.36-A
C     M=(3*TP*VM*BT)/K
C     WRITE(11,*)M
      X=(90*VM/K)-B
      N=-(X/M)-1
      A1=-(M/N)*(R**N)
      URBL=A1*(R**-N)*T
      WRITE(11,*)"M =",M,"X =",X,"N =",N,"A =",A,"URBL =",URBL
C     ------------BM-----------
      ROW=-(M/X)*R
      BBM=-(M/R)*ROW*EXP(R/ROW)
      URBM=BBM*EXP(-R/ROW)*T
      WRITE(11,*)"ROW =",ROW,"BBM =",BBM,"URBM =",URBM
C     ---------VERWEY-------
      G1=12
      MUE=-(M/G1)*(R**G1)
      URV=MUE*(R**-G1)*T
      WRITE(11,*)"MUE =",MUE,"URV =",URV
C     ---------VS--------
      K2=-(X/M-1)
      K3=2*(R**2)
      K1=K2/K3
      LAMDA1=M/(2*(R**2)*K1)
      LAMDA2=EXP(K1*(R**2))
      LAMDA=-LAMDA1*LAMDA2
      URVS1=LAMDA*T
      URVS2=EXP(-K1*(R**2))
      URVS=URVS1*URVS2
      WRITE(11,*)"LAMDA =",LAMDA,"URVS =",URVS,"K1 =",K1
C     ----------GT----------
      CONA=-X/(2*M)
      EP=SQRT(-7+4*CONA+4*(CONA**2))
      PK1=-1+2*CONA+EP
      PK2=4*(R**2)
      PK=PK1/PK2
      P0=EXP(PK*(R**2))
      P1=M*R*P0
      P2=2*PK*(R**2)+1
      P=-(P1/P2)
      URGT1=P/R
      URGT2=EXP(-PK*(R**2))
      URGT=URGT1*URGT2*T
C     WRITE(11,*)"P =",P,"PK =",PK,"URGT =",URGT
C     --------ISLAM--------
```

```
      MC=1-(1/SIG)-(X/(M*SIG))
      I=-M/(MC*SIG)*EXP(MC)
      URI=I*EXP(-MC)*T
C     WRITE(11,*)"MC =",MC,"I =",I,"URI =",URI
C     --------AK---------
      Z1=-X/M
      MC11=((SIG*SIG)-(7*SIG)+(Z1*SIG))
      MC12=SQRT((MC11**2)-(12*(SIG**2)*(4-Z1)))
      MC13=2*(SIG*SIG)
      MC1=(MC11+MC12)/MC13
      GA=M/(3+MC1*SIG)
      GB=(R**3)*EXP(MC1)
      G=-GA*GB
C     URAK1=EXP(-G2*(R**SIG))
      URAK=(G/(R**3))*EXP(-MC1)*T
C     WRITE(11,*)"URAK =",URAK,"MC1 =",MC1,"G =",G
C
C     Calculation of lattice Energy:-
C
      UE=(-440.18/R)*T
      UBL=UE+UVT+URBL
      UBM=UE+UVT+URBM
      UV=UE+UVT+URV
      UVS=UE+UVT+URVS
      UGT=UE+UVT+URGT
      UI=UE+UVT+URI
      UAK=UE+UVT+URAK
C     WRITE(11,*)"UE = ",UE
C     WRITE(11,*)"UBL= ",UBL
C     WRITE(11,*)"UBM= ",UBM
C     WRITE(11,*)"UV = ",UV
C     WRITE(11,*)"UVS= ",UVS
C     WRITE(11,*)"UGT= ",UGT
C     WRITE(11,*)"UI = ",UI
C     WRITE(11,*)"UAK= ",UAK
C
C     Calculation of pressure derivative of bulk moduli:-
C
C     --------BL-----------
      U21=-(880.36/(R**3))-(42*CV/(R**8))-(72*DV/(R**10))
      U22=N*(N+1)*A1*(R**-(N+2))
      U2=U21+U22
      U31=(2641.08/(R**4))+(336*CV/(R**9))+(720*DV/(R**11))
      U32=-N*(N+1)*(N+2)*A1*(R**-(N+3))
      U3=U31+U32
      BL=1-(R*U3)/(3*U2)
C     -------BM------------
      U42=(BBM/(ROW**2))*EXP(-R/ROW)
      U4=U42+U21
      U52=-(BBM/(ROW**3))*EXP(-R/ROW)
      U5=U52+U31
      BM=1-(R*U5)/(3*U4)
C     -------VERWEY--------
      U62=156*MUE*(R**-14)
      U6=U62+U21
      U72=-2184*MUE*(R**-15)
      U7=U72+U31
      BV=1-(R*U7)/(3*U6)
C     ---------VS----------
      U82=2*LAMDA*K1*EXP(-K1*(R**2))
      L1=4*LAMDA*K1*K1*R*EXP(-K1*(R**2))
      L2=L1*R
      U8=U21+U82+L2
      U92=(3*L1)-(2*L2*K1*R)
      U9=U31+U92
      BVS=1-((R*U9)/(3*U8))
```

```
---------BT
PHY=(P/R)*EXP(-PK*(R**2))
PH2=PHY/(R**2)
PH1=PHY/(R**3)
U10=U21+2*(1+PK*(R**2)+4*(PK**2)*(R**4))*PH2
U11=U31-(2*(3+(3*PK*(R*R))+(4*(PK**3)*(R**6)))*PH1)
BGT=1-(R*U11)/(3*U10)
WRITE(11,*)" BL=",BL," BM=",BM," BV=",BV," BVS=",BVS," BGT=",BGT
-----------ISLAM-------------
PHI=I*EXP(-MC)
PHI1=-SIG*(MC/R)*PHI
PHI21=-SIG*(MC/R)*PHI1
PHI22=-SIG*(SIG-1)*(MC/(R**2))*PHI
PHI2=PHI21+PHI22
PHI31=-SIG*(MC/R)*PHI2
PHI32=-2*SIG*(SIG-1)*(MC/(R**2))*PHI1
PHI33=-SIG*(SIG-1)*(SIG-2)*(MC/(R**3))*PHI
PHI3=PHI31+PHI32+PHI33
U12=U21+PHI2
U13=U31+PHI3
BI=1-((R*U13)/(3*U12))
WRITE(11,*)U12,U13,BI
----------------AK----------------
PHIA=(G/(R**3))*EXP(-MC1)
PHIA11=-3*PHIA/R
PHIA12=-(SIG*MC1*PHIA)/R
PHIA1=PHIA11+PHIA12
PHIA21=(12+(3*SIG*MC1))-(SIG*(SIG-4)*MC1)+((SIG**2)*(MC1**2))
PHIAK=PHIA/(R**2)
PHIA2=PHIA21*PHIAK
PHIA31=-(60+(12*SIG*MC1))
PHIA32=(3*SIG*(SIG-5)*MC1)-(3*(SIG**2)*(MC1**2))
PHIA33=-((SIG*(SIG-4)*(SIG-5)*MC1)-((SIG**2)*(SIG-4)*(MC1**2)))
PHIA34=((SIG**2)*(2*SIG-5)*(MC1**2))-((SIG**3)*(MC1**3))
PHIA3=(PHIA31+PHIA32+PHIA33+PHIA34)*PHIA/(R**3)
U14=U21+PHIA2
U15=U31+PHIA3
BAK=1-((R*U15)/(3*U14))
WRITE(11,*)"BAK=",BAK,"    BI=",BI
------------------------------------------------------------
DI1(IROW,01)=AP
DI1(IROW,02)=AN
DI1(IROW,03)=NP
DI1(IROW,04)=SPN
DI1(IROW,05)=SPP
DI1(IROW,06)=SNN
DI1(IROW,07)=TPP
DI1(IROW,08)=TNN
DI1(IROW,09)=TPN
DI1(IROW,10)=R
DI1(IROW,11)=VM
DI1(IROW,12)=BT
DI1(IROW,13)=K
DI1(IROW,14)=SIG
----------------------------------------------------------------------
DI2(IROW,01)=UVT
DI2(IROW,02)=URBL
DI2(IROW,03)=URBM
DI2(IROW,04)=URV
DI2(IROW,05)=URVS
DI2(IROW,06)=URGT
DI2(IROW,07)=URI
DI2(IROW,08)=URAK
DI2(IROW,09)=UBL
DI2(IROW,10)=UBM
DI2(IROW,11)=UV
```

```
            DI2(IROW,12)=UVS
            DI2(IROW,13)=UCT
            DI2(IROW,14)=UI
            DI2(IROW,15)=UAK
            DI2(IROW,16)=BL
            DI2(IROW,17)=BM
            DI2(IROW,18)=BV
            DI2(IROW,19)=BVS
            DI2(IROW,20)=BCT
            DI2(IROW,21)=BI
            DI2(IROW,22)=BAK
10000       CONTINUE
C           ------------------------------------------------------------
            DO 1002 IROW=1,4
              WRITE(33,200) COMP,(DI2(IROW,JCOL),JCOL=1,22)
 1002       CONTINUE
C           ------------------------------------------------------------
00100       FORMAT((A),14F7.0)
00200       FORMAT((A),4X,11F11.3/8X,11F11.3/)
00998       FORMAT (A)
            STOP
            END
```

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