

The Study of Vander Waals (vdW) Coefficients for Chalcogenide Semiconductor Compound (ChSCs)

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Abstract:- The *vdW* equation is an equation of state that can be derived from a special form of the potential between a pair of molecules (hard-sphere repulsion and r^{-6} *vdW* attraction). The *vdW* force (or *vdW* interaction), named after Dutch Scientist Johannes Diderik van der Waals, is the attractive or repulsive force between the molecules (or between parts of the same molecule) other than those due to the covalent bonds or the electrostatic interaction of ions with one another or with neutral molecules. The investigation of physical properties of the crystals depends on the motion of the constituent atoms (or ions) and requires the knowledge of actual form of the phonon frequency spectrum, which can be achieved from the theoretical models of lattice dynamics. The efforts have been made to develop a series of lattice dynamical models, which have progressed rapidly through the simple phenomenological to the sophisticated microscopic approaches. The energy is written as a function of a single lattice constant and the structure has been determined by minimizing the energy with respect to this parameter. These are the total electron density which is the sum of the two separate densities and the non Coloumbic part of the interaction potential may be evaluated by an electron gas treatment. It has been found that the *vdW* interactions are quite important in the calculation of cohesive energies of different crystal structures [10]. The prediction of relative stability and phase transition depends appreciably on the accuracy of determining the *vdW* coefficients (c_{kk} and d_{kk}). In this study evaluation of The Study of Vander Waals (vdW) coefficients for Chalcogenide Semiconductor compound (ChSCs) is been made and result is recorded which can be used as reference for many future studies. In the present study of mixed *Chalcogenide semiconductor Compounds (ChSCs)*. We have used the Hafemeister and Flygare (*HF*) type potential which allows us to extend the overlap repulsion up to second neighbour ions. In the present study the values of $c_{/A}$ obtained from *SKV* approach have been used for the evaluation of *vdW* energies.

Introduction

The *vdW* forces were in *first postulated* the study of equation of state for rare gases and are responsible for the atoms of a crystal. In terms of classical picture these weak attractive forces arises as a consequence of the fact that an electron revolving around a nucleus may be considered to represent a rotating electric dipole.

The *vdW* interaction term includes:

- * Permanent dipole-permanent dipole forces
- * Permanent dipole—induced dipole forces
- * Instantaneous induced dipole-induced dipole (London dispersion forces).

In order to keep the molecules held together, there exist two types of bonds i.e. strong and weak bonds. The bonds, which hold atoms together to form molecules, are often called as strong bonds. The term weak bonds refer to an attachment between molecules due to simple electrostatic attraction, such as between the polar energies are typically in the range *0.04to 0.3eV*. Weak

bonds are generally the result of attraction between the dipoles. The Physical Origin of interactions is connected with the correlation of electronic motions in different atoms and can actually be understood in semi classical terms. Now, what is a dipole? Single point charge is called a monopole. An arrangement of and opposite charges separated by a very small distance is called a dipole. The 2 shows two molecules A and B that have permanent dipole moment attracting each other. Besides such dipole-dipole bonds, there can be induced dipole moment in nonpolar molecule. An arrangement of four charges with small separation of charges is termed as quadrupole.

The *vdW* interaction is a weak force. When two atoms or molecules approach each other, there is a weak attraction between them long before their electron clouds can overlap appreciably. This attraction can be considered as a manifestation of various effects, such as the electrostatic interaction between the charge distributions of the two atoms the mutual polarization whereby each charge could induce slight charge in the other and the dispersion forces

which are the result of a random fluctuating polarization occurring due to the random movement of electrons. All these forces are relatively weak and are masked by strong covalent or repulsive forces at inter-nuclear distances existing in Compounds..

From the mathematical analysis of the forces acting between neutral atoms it follows les the dipole- dipole interactions there are higher order interactions of the type -quadrupole, quadrupole - quadrupole etc. All these together are referred to as *vdW* interaction. Now, let us focus us on the dipole-dipole and dipole-quadrupole interactions, taken into consideration. When two atoms are so far apart that there is negligible of their charge clouds, the atoms although neutral and non-polar interact through a Electrostatic multipole terms. The most important one is the lowest order dipole-dipole term. An instantaneous electric dipole moment in one atom, which averages to zero, induces His moment in other atom, which is proportional to the induced moment and which interacts with it. It is readily seen that the interaction energy varies as r^{-6} and does not average to zero, and corresponds to an attraction between atoms. The *vdW* attraction to dipole-dipole interaction between neutral atoms at atomic distances is of the order of 10^{-2} eV. The dipole-dipole term provides the explanation for the imermolecular attractive forces [18]. Similarly, an instantaneous electric quadrupole in one atom induces a dipole moment in the other, which interacts with it to give the interaction energy varying as r^{-8} , which is called dipole-quadrupole term. Also, the interaction between quadrupole-quadrupole (*q-q*) results a weak interaction varying as r^{-10} , which we generally neglect due to its small magnitude.

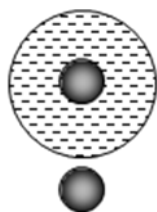


Figure 1 (a) Uniform distribution of an atom charge

Thus the potential due to *vdW* interaction can be written as,

$$\Phi_{v(r)} = \sum c_{kk'} r_{kk'}^{-6} + \sum c_{kk'} r_{kk'}^{-8} \tag{1}$$

where, $c_{kk'}$ and $d_{kk'}$ are the *vdW* coefficients due to the dipole -dipole (*d-d*) and dipole-quadrupole (*d-q*) interactions, $r_{kk'}$ is the separation between k^{th} and k'^{th} ions. On simplification this ultimately gives:

$$\Phi_v(r) = -Cr^{-6} - Dr^{-8} \tag{2}$$

Here the overall *vdW* coefficients *C* and *D* are then expressed in terms of $c^{kk'}$ and $d^{kk'}$, by an appropriate lattice sums ($S_{kk'}$ and $T_{kk'}$) the values of which are taken from Tosi [8] such that and the expressions for *C* and *D* are given by,

$$C = c_{kk'} S_{kk'} + c_{kk} S_{kk} + c_{kk} S_{kk} \tag{3}$$

$$D = d_{kk'} T_{kk'} + d_{kk} T_{kk} + d_{kk} T_{kk} \tag{4}$$

Evaluation of the *VdW* coefficients

The *vdW* coefficients for mixed system of ionic crystals can be evaluated by using two methods, (a) Perturbation method suggested by Mayer [4] long back and (b) *SKV* method [13] developed by Narayan [30], which is superior to perturbation theory of London [5] and Margenau [31]. In the former method these coefficients are read as.

$$c_{kk'} = \frac{3}{2} \alpha_k \alpha_{k'} \frac{E_k E_{k'}}{E_k + E_{k'}} \tag{5}$$

$$d_{kk} = \frac{9}{4} \frac{C_{kk}}{e^2} \left[\frac{\alpha_k E_k}{N_k} + \frac{\alpha_k E_k}{N_k} \right] \tag{6}$$

Where *a* is the polarizability, *E* is the excitation energy parameter and *N* is the effective number of electrons. However the derived coefficients are highly unreliable as discussed by Narayan [15] and others [12]. In the variational methods [13,30] these coefficients are read as

$$C_{kk} = \frac{3}{2} \frac{e\hbar}{m^{1/2}} \frac{\alpha_k \alpha_k}{(\alpha_k/N_k) + (\alpha_k/N_k)} \tag{7}$$

$$C_{kk} = \frac{27\hbar^2}{8m} \alpha_k \alpha_k \frac{[(\alpha_k/N_k) + (\alpha_k/N_k)]}{[(\alpha_k/N_k) + \frac{2\alpha}{3}(\alpha_k \alpha_k / N_k N_k) + \alpha_k / N_k]} \tag{8}$$

Since *SKV* method does not use the excitation energies, the coefficients calculated by this method are much accurate.. Thus, the evaluation of *vdW* coefficients from the *SKV* method makes use of the effective number of electrons and therefore does not involve uncertainties. On the other hand, the expressions force .and *d* .derived from the perturbation theory involve certain parameters such as excitation energy whose estimation has many uncertainties.

Overlap Repulsive Interaction Potential $\Phi_R(r)$:

In the earlier sections, we have discussed the Coulomb and *vdW* interactions, which are attractive in nature between the ions, and form a crystal. In order to

prevent these ions from collapsing, the existence of a repulsive interaction is essential to keep the ions at some distance apart to form a crystal structure. What is SR repulsion? The volume of matter in the solid and liquid states is an extensive property i.e. it is proportional to the number of moles or molecules in the specimen. This implies a molecular size or the existence of repulsive force that prevents two molecules from occupying the same space at the same time. The very low compressibility of solids and liquids indicate a strong repulsion of two molecules when they begin to overlap each other. These self-evident conceptions were embodied in the nineteenth century representation of molecules as little billiard balls. The origin of the overlap forces of repulsion was not explained until the advent of quantum mechanics and the Pauli's exclusion principle. Accordingly, when two noble gas atoms begin.

Overlap, the electrons tend to migrate from the crowded region in the middle to the far outside the nuclei, where they exert electrostatic forces that tend to pull nuclei apart. This effect, which greatly exceeds the direct electrostatic repulsion of the partially shielded nuclei, cannot be represented by any simple analytic potential energy function [26].

The atoms in a mixed system of *Chalcogenide semiconductors compounds (ChSCs)* are at sufficiently close separation and hence their charge distributions overlap appreciably. The overlap energy is repulsive and arises mainly due to the Pauli Exclusion Principle. The functional form of the repulsive potential is difficult to evaluate from first principles methods. Although some quantum-mechanical calculations of the repulsive interaction have been carried out but its application has been restricted to ionic solids. Semi-empirical forms for the SR requirements had led to the adoption of either inverse power potential or exponential decaying potential i.e.

$$\Phi_R(r) = Ar^{-n}$$

9

$$\Phi_R(r) = B \exp(-r/p)$$

10

Proposed by Born and Born-Mayer respectively. This potential is more realistic and suitable for computations. They observed that the exponential potential gives

most satisfactory agreement with the experimental results than the inverse form. A detailed account of the repulsive potentials has been presented by Tost [8]. The B-M potential was further developed by Fumi and Tosi [35] for the better description of the overlap repulsive energy by including the second neighbour interaction given as,

$$\Phi_{kk'}(r) = b\beta_{kk'} \exp\left(\frac{r_k+r_{k'}}{\rho}\right) \quad 11$$

Here, b and ρ are the hardness (strength) and range parameters: r_k and $r_{k'}$ are the ionic radii k and k' ions and β are the Pauling coefficients defined as,

$$\beta_{kk'} = 1 + \left(\frac{Z_k}{N_k}\right) + \left(\frac{Z_{k'}}{N_{k'}}\right) \quad 12$$

Where, Z_k ($Z_{k'}$) and N_k , ($N_{k'}$) are the valency and number of electrons in the outermost orbit. A detailed account of the static properties in solids or liquid crystals has been given by fumi and Tosi [35]. In order to describe the overlap repulsive energy in a better way several ramification of *B-M* potential were developed. Up till now several forms of *SR* repulsive potentials have been reported by number of researchers. A few well-known *SR* repulsive potentials are the Mayer and Huggins [16] Fumi-Tosi [11]. Hafemeister and Flygare (*HF*) [17] and Hafemeister and Zahrt (*HZ*) [18]. These workers have extended the *B - M* potential by including the effect of the second neighbour interactions without any additional parameter.

This form also includes the concept of ionic radii as introduced in the modified Born-Mayer potential. Such type of concept are originated from the observed approximate additivity of the interatomic distance in a family of salts of a given substance which implies that the inter-ionic distance $r=r_k+r_{k'}+\Delta$ (where r_k and $r_{k'}$ are the radii of +ve and -ve ions respectively and Δ varies from crystal to crystal). Thus the expression for *HF* type repulsive representing *SR* interaction energy is

$$\Phi_{kk'}(r) = \sum_{kk'} b\beta_{kk'} \exp\left(\frac{r_k+r_{k'}}{\rho}\right) \quad 13$$

where $r_{kk'}$ is the first and $r_{kk}=r_{k'k'}$ is the second neighbour separations, respectively. On simplification this ultimately gives

$$\Phi_R(r) = nb\beta_{kk'} \exp\left(\frac{r_k+r_{k'}-r}{\rho}\right) + n\frac{b}{2}\beta_{kk'} \exp\left(\frac{2r_2-k_r}{\rho}\right) + n\frac{b}{2}\beta_{kk'} \exp\left(\frac{2r_2-k_r}{\rho}\right) \quad 14$$

Result and Conclusion

This paper aims to review the crystal interactions and mechanism of binary solids is progressing. The progression traced in literature has witnessed the development of several interactions potential and lattice mechanical models on the basis of simple phenomenological and sophisticated microscopic theories. It is now applied in the present study to test its validity under the situations of appreciable change in the inter ionic distance due to high pressure ; here we are using TBFP model which is selected for the present study to widen its area of applicability. The TBFP parameters have been by a prior approach and therefore the model is more sophisticated and realistic than any other models.

Table 1 Values of Lattice Sums of vdW Coefficients

Solids	NaCl(B1)	CsCl(B2)	ZnS(B3)
S_{kk}	0.9034	1.7723	0.3811
$S_{kk'}$	6.5952	8.7088	4.3544
$S_{k'k''}$	0.9034	1.7723	0.3811
T_{kk}	0.4000	1.0989	0.1266
$T_{kk'}$	601457	8.1575	4.0787
$T_{k'k'}$	0.4000	1.0989	0.1266

Table 2 Calculated values of vdW coefficients for ChSCs

	C_{ii}	C_{ij}	C_{jj}	D_{ii}	D_{ij}	D_{jj}	C		D	
							B_1	B_3	B_1	B_3
ZnS	177.25	572.92	2352.42	480.49	4760.81	17297.69	6063.84	3458.79	36369.80	21668.65
ZnSe	177.25	659.30	3287.61	480.49	6280.41	27027.63	7478.34	4191.29	49600.75	29098.43
ZnTe	177.25	805.34	5348.97	480.49	9473.38	51720.38	10303.78	5612.82	79100.89	45247.70
CdS	1639.22	1937.52	2352.42	8678.87	16361.76	17297.69	16384.36	9957.94	110945.08	70023.34
CdSe	1639.22	2266.37	3287.61	8678.87	20889.79	27027.63	19398.07	11746.30	142664.97	89723.62
CdTe	1639.22	2831.73	5348.97	8678.87	30116.75	51720.38	24988.99	14993.71	209248.22	130483.74
HgS	5079.62	3448.47	2352.42	32505.53	30974.96	17297.69	29457.44	17848.36	210284.07	132642.64
HgSe	5079.62	4054.69	3287.61	32505.53	39140.17	27027.63	34300.44	20844.49	264357.01	167177.91
HgTe	5079.62	5103.48	5348.97	32505.53	55606.05	51720.38	43079.67	26196.93	375428.45	237463.38

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