

Study of cohesive energy for KX ($X=F, Cl, Br \& I$) crystal structure

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The cohesive energy of the potassium halides has been calculated for different assumed form for the interaction potential energy. In the present paper the three-body force shell model (TBFSM) have been used for calculation of cohesive energy of KX ($X=F, Cl, Br \& I$) crystal. The used model has found to posses some remarkable features. The nearest and next-nearest neighbour interactions as well as van der Waals interactions are taken into account to evaluate the cohesive energy that has given good agreement with experimental results. The value of cohesive energy already performed By Sharma [1] but some error has been found .So by use of present model we can out com from such error. In the present paper value of cohesive energy also compared with Sarkar & Sengupta [2] and with three-body potential by Basu & sengupta [3].The atomization energy also reported for potassium halides crystal by using the value of cohesive energy. The obtained results are found to be in close agreement with experimental result.

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1. Introduction

Solids have stable structures, and therefore it exist interactions holding atoms in a crystal together. NaCl type crystal structure which is more stable than a collection of free Na and Cl atoms. It implies that the Na and Cl atoms attract each other, i.e. there exist an attractive interatomic force, which holds the atoms together. This also implies that the energy of the crystal is lower than the energy of the free atoms. The amount of energy, which is required to pull the crystal apart into a set of free atoms, is called the cohesive or dissociation energy of the crystal.

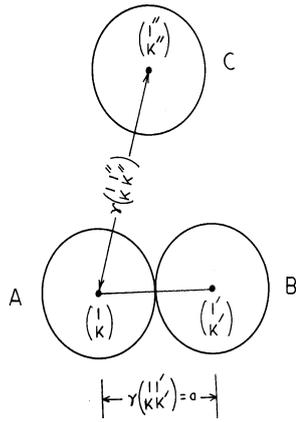
Cohesive energy = energy of free atoms –crystal energy

Magnitude of the cohesive energy varies for different solids from 1 to 10 eV/atom, except inert gases in which the cohesive energy is of the order of 0.1eV/atom. As for as cohesive energy is concerned the charge –charge and overlap terms are most important. The cohesive energy controls the melting temperature. The cohesive energy and other properties of alkali halide crystal have been calculated by assuming different forms for potential energy function. The important interactions are electrostatics, Van der Waals forces, overlap and polarization. Inclusion of all these interaction terms makes the potential function fairly complicated. The three-body force shell models (TBFSM) have developed by Verma & Singh [4] by including the charge transfer mechanism in the framework of Rigid Shell model (RSM). Its development is based on the postulate that when the two ions come closer to each other during lattice vibrations,

their electron shells overlap and the spherical distribution is deformed. This deformation leads to the appearance of multipoles. If a third ion is present near the former two ions, the charge of the shells of the third ion interacts with these multi poles. This multi pole-charge interaction recognized as the many-body interaction whose FC three-body components seem to play the most dominant role. The existence of three-body interactions (TBI) have very well established by Lowdin [5] and Lundqvist [6]. An expression for the contribution of TBI to the dynamical matrix has been rigorously derive and exactly evaluated by Verma & Singh [4] for NaCl-structure and by Lal & Verma [7] for CsCl- structure.

1.1. Theory of TBI

According to quantum-mechanical theory using Heitler London approximation [8], the atomic wave functions are treated rigidly connected with their nuclei and supposed not to change in a deformation of the lattices. These effects lead to the non-orthogonality of the one-electron wave functions. As a natural consequence of the anti symmetry requirement on the wave function [8], this alteration in the electronic charge density causes a charge depletion which depends on the inter nuclear separation and interacts with all other charges via Coulomb force law and give rise to long-range TBI introduced by Lowdin[5] and Lundqvist [6].



[Ionic Charges of A & B and third distant ion C modifies and produces three-body forces on them]

Let us consider a number of atoms or ions at the sites $L=1, 2$ etc. At every site L we have positive nucleus of charge $\epsilon_L e$ and number n_L of electrons such that $Z_L (= \epsilon_L - n_L)$ is the net ionic charge at L . The number density $n(\vec{r})$ of electrons in the crystal can be expressed as:

$$n(\vec{r}) = \sum_L n_L(\vec{r}) + \Delta n(\vec{r}) \quad (1)$$

Here $n_L(\vec{r}) \{ = \epsilon_L e \delta(\vec{r} - \vec{r}_L) \}$ represents the electron distribution in a free ion at the position L and $\Delta n(\vec{r})$ gives the deviations from the distribution. According to Lundqvist, identical to the overlap integrals. Its value is given by

$$P_{\mu\nu} = S_{\mu\nu} - \sum_{\delta} S_{\mu\delta} S_{\delta\nu} S_{\mu\nu} \quad (2)$$

$$\text{where, } S_{\mu\nu} = \int \psi_{\mu}^*(x) \psi_{\nu}(x) d\tau \quad (3)$$

Here, ψ_{μ} are the normalized one-electron wave-functions including spin such that $x=(r, \xi)$; the index μ refers to an electron with quantum numbers n, l, m and ξ associated with an ion at a certain lattice point L_{μ} . The expression for the modified Coulomb energy for the whole crystal can be written as:

$$\Phi_m^c = 1/2 \sum_{lk} \sum_{l''k''} \Phi_m^c \{ r(lk, l''k'') \} \quad (4)$$

$$\Phi_m^c = \Phi^c + \Phi^T$$

where the first term is the well known Coulomb potential. The second term is purely TBI energy given by:

$$\Phi^T = e^2 \sum_{lk} \sum_{l'k'} \sum_{l''k''} Z_k f \{ r(lk, l'k') \} \frac{Z_k''}{|\vec{r}(lk, l''k'')|} \quad (5)$$

in Eqn. (5) it is clearly indicate that the inclusion of TBI modifies the Coulomb part of classical energy by a factor $\{1+(2n/Z) f(r)\}_0$. In NaCl-type lattice, since each ion is

surrounded by six nearest - neighbours of opposite type, therefore, the modified ionic charge becomes [16] $Z_m e = \pm (Z+6f_0)e$. The TBFSM described above has been extensively applied by Singh & Verma [4,10] and their associates to describe successfully lattice dynamics of alkali halides [4,10,11]. The effects of TBI on the cohesive energy of ion crystals have been investigated by Sharma et al.[1] and Singh and Nirwal [12,13]. The effects of TBI have been found to be important in the study of lattice dynamics of rare gas solids [14, 15].

1.2 Coulomb interaction potential

The Coulomb interaction potential is long-range in nature an ionic crystal to consist of N -positive and N -negative ions separated by a distance $|\vec{r}_{ij}|$, where \vec{r}_{ij} is a vector joining the ions i and j . where the prime means summation over all ions except $i=j$, ϵ_{ij} will be $+1$, if i and j are like ions and -1 , if they are unlike, e is the electronic charge. Thus, the Coulomb potential energy for the whole crystal is given by

$$\Phi^c(r_0) = N\Phi^c(r_0) = \sum_{n_1, n_2, n_3} \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \cdot \frac{e^2}{r_0} \quad (6)$$

where n_1, n_2, n_3 are the integers and r_0 is the equilibrium nearest neighbour distance.

1.3 The repulsive potential

The most commonly used analytical expression for the repulsive energy are given by the inverse and exponential power laws such that

$$\Phi^R(r_{ij}) = A r_{ij}^{-n} \text{ (Born Potential)} \quad (7)$$

$$\Phi^R(r_{ij}) = b \exp(-r_{ij} / \rho) \text{ (Born-Mayer Potential)} \quad (8)$$

Where A (or b) and n (or ρ) are the Born exponents called the strength and hardness parameters, respectively. In order to take explicit account of the B-M repulsion of the second-neighbours in the ionic crystal, a possible extension of the expression (8) to the second-neighbour yields the repulsive energy [17,18].

$$\Phi^R = M\beta_{+-} b \exp[(r_+ + r_- - r)/\rho] + 1/2M'b [\beta_{++} \exp(2r_+/\rho) + \beta_{--} \exp(2r_-/\rho)] \exp(-r'/\rho) \quad (9)$$

where M and M' are the number of first and second-neighbours and r' is the distance between the second neighbours. β_{ij} are the Pauling coefficients known compressibility factor [17,18]. Thus potential parameters in the case of Born-Mayer potential for NaCl type structure given as

$$\rho = \left[2 + \frac{18r_0^4}{\alpha\beta e^2} \right]^{-1} \quad (10)$$

Here r_0 is the nearest neighbors distance in the lattice at equilibrium is the Madelung's constants and e is electronic charge.

1.4 Van der Waals potential

The instantaneous dipole moment of a closed shell atom induces a dipole moment on a similar atom and the interaction energy thus arising is known as the van der Waals interaction (VWI) potential denoted by $\Phi^v(r)$. The potential energy due to these two dipole moments parallel to each other is given by

$$\Phi_{dd}^v(r) = -\frac{2\mu_1\mu_2}{r^3} = -\frac{4\alpha\mu_1^2}{r^6} = -\frac{c}{r^6} \quad (11)$$

According to the quantum theory of perturbation [19,20], VW energy due to d-d and d-q interactions is expressed as:

$$\Phi_{dd}^v(r_{ij}) = -\frac{3}{2} \alpha_i \alpha_j \frac{E_i E_j}{E_i + E_j} \cdot \frac{1}{r_{ij}^6} = -\frac{c_{ij}}{r_{ij}^6} \quad (12)$$

$$\Phi_{dq}^v(r_{ij}) = -\frac{4}{9} \frac{c_{ij}}{e^2} \left[\frac{\alpha_i E_i}{n_i} + \frac{\alpha_j E_j}{n_j} \right] \cdot \frac{1}{r_{ij}^8} = -\frac{d_{ij}}{r_{ij}^8} \quad (13)$$

where α_i and α_j are the crystal electronic polarizabilities of the i and j ions, respectively. E_i and E_j are the appropriate excitation energy parameters; n_i and n_j are the effective number of electrons in the ions necessary to account for the actual polarizabilities; c_{ij} and d_{ij} are constants. The cohesive energy per unit cell at nearest neighbor r ,

$$\phi(r) = \frac{\alpha_M e^2}{r} + 6be^{-\frac{r}{\ell}} + \frac{6\alpha_M e^2}{r} f(r) + \frac{c}{r^6} \quad (14)$$

Where e is electronic charge; r_{ij} are the interionic separation and van der Waal coefficient defined by c . The cohesive energy per mole is calculated by.

$$W = -[N\phi(r) + \varepsilon_0], \quad (15)$$

where N as the Avogadro number and ε_0 is the zero point energy per mole. The calculated Zero -point energy with vdW and TBI have been given by [12].

$$E_{Zeropoint} = \frac{1}{2} \sum_{i,q} \hbar \nu_0(j,q) \quad (16)$$

Here \hbar is plank's constant and vibrational frequency for zero point is ν_0 .

Values enclosed in () represent deviation between experimental and theoretical results. The study about the stability of crystals known well by atomization energy so we have calculated the atomization energy

$$C = \Phi + C' - I \quad (17)$$

Where C is atomization energy, C' and I are the electron affinity of anions and ionization energy of cations respectively.

2. Result and discussion

The binding in ionic crystals have been explained by calculating their cohesive energy from a large number of interatomic interaction potentials. The potentials are adequately successful to describe the lattice static and dynamic properties of perfect and defect ionic crystals. The calculated cohesive energy by using TBI much better reproduction that reported by [1] whose result have been large deviation approx 15%. From Fig. 1 comparative graph for cohesive energy shows the betterment of present model. After inclusion of vdW with TBI good agreement established between theoretical and experimental result given in Table-1. By using atomization energy graphs from Fig. 2 it shows that for KF atomization energy value is low using the value of cohesive energy reported by Sharma [1] but very low for sarkar [2] and for other values KI, KCl and KBr, appearing deviations are within the range of 10% and it shows the accuracy of present model to describe the cohesive energy and stability for potassium halides. The calculated atomization energies by using present model in Table2 has given excellent agreement with experimental data. The other important structural properties of potassium halides and other alkali halides crystal reported by different researchers [24-31] that will be helpful for complete theoretical investigation about alkali halide crystals.

Table 1. Cohesive energy of Potassium Halides in (kcal/mole).

Crystal	Calculated Cohesive energy with [TBFSM]		Calculated Cohesive energy with vdW and TBFSM		Experimental Values [21]
	SHARMA et al [1]	Present Work	SARKAR & SENGUPTA [2]	Present Work	
KF	177.1(-6)	180.5	-----	179.7	189.8 (194.5)
KI	112.0(-25)	137.5 (-7.0)	154.0	146.3	149.9 (151.1)
KCl	143.7(-13)	160.3 (-4.1)	171.3	154.9	165.8 (169.5)
KBr	129.2(-18)	140.2 (-5.1)	163.5	152.6	158.5 (159.3)

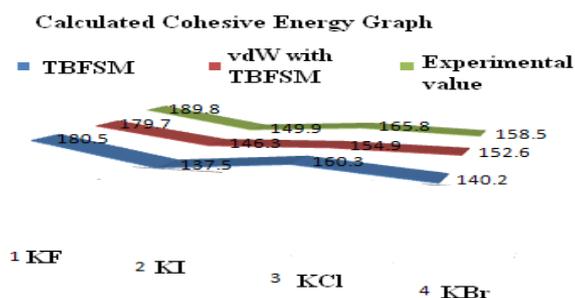


Fig. 1. Cohesive energy of Potassium Halides in Kcal/mole.

Table 2. Atomization energy (kcal/mole) of potassium halides.

Crystal	Atomization energy value Experimental		Calc. atomization energy with vdW and TBFSM	Atomization energy using value of	Atomization energy using value of
	C Ref. [22]	I Ref [23]	Present Work	Sharma et al [1]	Sarkar & Sengupta [2]
KF	79.5	100.0	159.2	156.5	20.5
KI	70.6	100.0	116.3	82.6	124
KCl	83.2	100.0	138.1	126.9	154.3
KBr	77.5	100.0	130.1	106.7	141

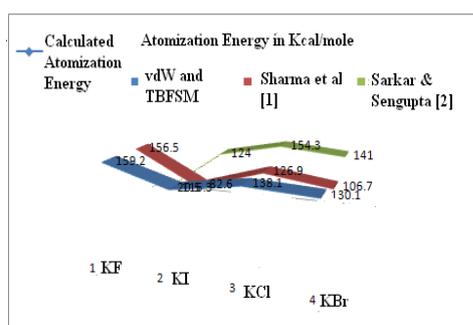


Fig. 2. Calculated Atomization Energy for KF, KI, KCl and KBr.

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