

Effect of many body interactions on cohesive energy of alkali halides

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ABSTRACT

The deviations between calculated and measured values of cohesive properties of alkali halides have motivated us to frame a model for calculating the same for rock salt structure alkali halides. The present approach shall include the effect of many body Coulombian, Born-Mayer type overlap repulsive and Van Der Waals (vdw) interactions in the framework of Rigid Shell Model (R.S.M.). We hope that our results will show excellent agreement with measured cohesive energies for all the alkali halides. Further we will compare our result with atomization energy.

Key words: Cohesive energy, Alkali halides and atomization energy.

INTRODUCTION

There has been always a continuing effort to obtain accurate interatomic potential functions. The interaction potential energy function is generally used to study the crystalline properties of diatomic crystal like alkali halides. The first alkali halide potential, which gave a good fit to the lattice energy were obtained by Huggins and Mayer in 1933¹. The total potential⁷ for the alkali halides can be written as

$$\Phi = \Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VWI} \quad \dots(1)$$

When first term Φ^C is coulomb interaction potential and is long-range in nature, second term is Φ^R short-range overlap repulsion potential, third term Φ^{TBI} is three-body interactions potential and the last term is Φ^{VWI} Vander Waals interaction potential and owes its origin to the correlations of the electron motions in different atoms. We consider that Vander Waals energy converges fast but the overlap repulsion converges much faster. Therefore, the overlap repulsion is effective only up to the first neighbour and the Vander Waals attraction up to the second neighbour. Several workers have

calculated the cohesive energy of alkali halides using different model potentials³⁻⁴ but none could explain the experimentally measure values successfully. The present approach shall include the effect of many-body, Coulombian, Born-Mayer type overlap repulsive and van der Waals [vdw] interactions in the frame work of rigid shell model (RSM)⁷. The aims of the present work are two fold. Firstly, we shall introduce many body interactions [MBI] in the manner^{2,7-10}. Instead of coulomb interactions and Born-Mayer type overlap repulsive interactions⁵, secondly we also included van der Waals, interaction and zero point energy. This will improve the result remarkably. The calculation will be performed with and without the inclusion of vdW interactions. The results will be compared with the available experimental data for all alkali halides. Finally we will compare the cohesive energy with atomization energy because the atomization energy provides reliable information about the relative stability of crystal structures.

Theory

It is well known that the ions during lattice vibrations suffer an appreciable overlap and consequently their electron shells undergo

Three-body interactions

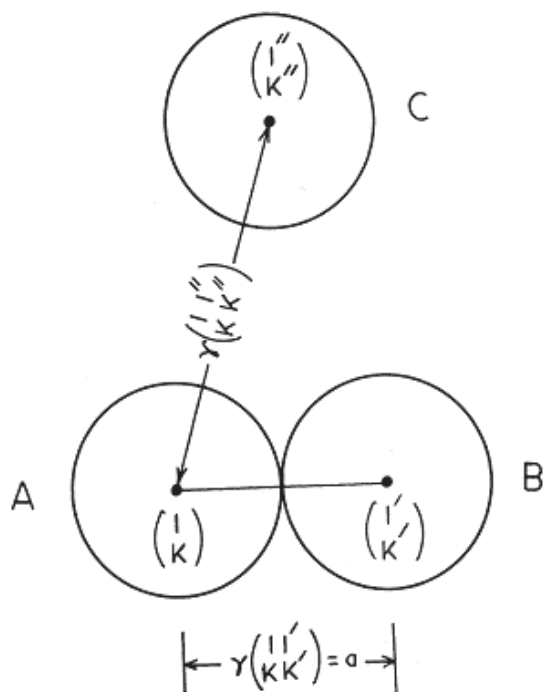


Fig. 1: When the two neighbouring ions a and b come closer to each other, overlapping of the electron charge clouds result in a net change in charge on both of them. Likewise, the presence of third distant ion c also modifies the ionic charges of a and b and produces three-body force on them.

deformation. This mechanism causes a transfer of charge between the overlapping adjacent ions. These transferred charges, in turn, interact via their associated Coulomb field with all other charges of the lattice and give rise to the long-range many-body interactions (MBI)²⁰ whose most significant component is the three-body interaction (TBI). The origin of these (TBI) has been well established from the classical as well as quantum mechanical theories. A brief account of their treatment is given below.

In Order to understand the existence of TBI from the charge transfer mechanism, let us consider the ions A,B and C represented by (I, k) , (I', k') and

(I'', k'') , respectively in an ionic crystal [Fig. (1.1)] having ionic charge $\pm Ze$. Here B is the nearest neighbour (nn) of A separated by a distance $|\vec{r}(I, k, I', k')|$ and C as any ion at a distance apart from A. The electron shells of ions A and B overlap during lattice vibrations and give rise to the transfer of a charge

$$dq_k = + Zef_k \{r(I, k, I', k')\} = \pm Zef_k(r) \dots (1)$$

Whose amount depends on the degree of overlap, i.e., interatomic separation (r) ; $f_k(r)$ is a function which is significant only between nearest neighbour ions and is expressed as $f_k(r) = (Z_k/Z) f(r)$, where $Z=|Z_k|$.

The occurrence of above transferred charge leads to a modified ionic charge:

$$Z_k e = Z_k e + nef_k \{r(I, k, I', k')\} = \pm Z_k e \left[1 + 2n/Z f \{r(I, k, I', k')\} \right]^{1/2}$$

Here, n is the number of nearest neighbour ions and $[1 + \{n/2\} f(r)]^2$ have been approximated as $[1 + 2n/Z f(r)]^{1/2}$ in view of smallness of $f(r)$. On similar arguments, we express the total charge on ion C as

$$Z_{\text{net}} e = \pm Z_k e \left[1 + 2n/Z f \{r(I'', k'', I''', k''')\} \right]^{1/2} \dots (3)$$

Where (I''', k''') ion is not shown in Fig. (1.1), but denotes the nn ion of C.

In view of the above descriptions, the Coulomb interaction energy between ion-pairs A and C gets modified and its expression is given by:

$$\begin{aligned} \Phi_{AC} \{r(I, k, I'', k'')\} &= e^2 \left[\frac{Z_k}{|\vec{r}(I, k, I'', k'')|} + \frac{n e^2}{|\vec{r}(I, k, I'', k'')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \right] \right] \right] \times \\ &= \frac{Z_k Z_{\text{net}} e^2}{|\vec{r}(I, k, I'', k'')|} + \frac{n e^2}{|\vec{r}(I, k, I'', k'')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \right] \right] \times \\ &= \frac{Z_k Z_{\text{net}} e^2}{|\vec{r}(I, k, I'', k'')|} + \frac{n e^2}{|\vec{r}(I, k, I'', k'')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \right] \right] \times \\ &= \frac{Z_k Z_{\text{net}} e^2}{|\vec{r}(I, k, I'', k'')|} + \frac{n e^2}{|\vec{r}(I, k, I'', k'')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \left[\frac{Z_k}{|\vec{r}(I, k, I', k')|} + \frac{n e^2}{|\vec{r}(I, k, I', k')|} \right] \right] \times \dots (4) \end{aligned}$$

Here, the first term is the well known two-body Coulomb potential. The second-term contains two parts specifying the contributions whose magnitude depends on the co-ordinates of three atoms and hence they are referred to as three-body interactions. The last term represents a contribution due to four-body interactions and is neglected in view of its smallness being a product of too small functions. Since the ion pairs are identical through the crystal, therefore, the same function $f\{r(lk, l'k')\}$ can be used to represent the charge-transfer between each ion pairs.

The expression for the modified Coulomb energy for the whole crystal can be written as:

$$\Phi_m^c = 1/2 \sum_k \sum_{l'l''k''} \Phi_m^c \{r(lk, l'l''k'')\} \\ = \frac{e^2}{2} \sum_k \sum_{l'l''k''} \frac{Z_k Z_{k'}}{\bar{r}(lk, l'l''k'')} \left[1 + \frac{2n}{Z} f\{r(lk, l'l''k')\} \right] \dots (5)$$

$$\Phi_m^c = \Phi^c + \Phi^T \dots (6)$$

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

$$\Phi^T = e^2 \sum_k \sum_{l'l''k''} \sum_{l'l''k''} Z_k f\{r(lk, l'l''k')\} \frac{Z_{k'}}{\bar{r}(lk, l'l''k'')} \dots (7)$$

The occurrence of Coulomb attraction is understood easily from an electron transfer point of view. The repulsive part of these potentials is inverse power or exponential function. A reasonably good description of both the attractive and repulsive interactions in ionic solids is given by Born and Mayer (BM) potential¹.

According to the quantum theory of cohesion, the ionic crystals possess Vander Waals and many-body interactions. The former contribution to the energy is mainly due to dipole-dipole interaction. The most significant component of the latter contribution is only the three-body interactions (TBI). Quantum mechanically, there occur lattice vibrations even at absolute zero temperature and lead to the zero-point energy of the crystals.

Thus, the zero-point energy contribution must also be included along with other contributions.

Van der Waals Potential

In addition to the Coulomb attraction described earlier, there exists another attraction between the closed shell atoms. The nature of this attraction is different and owes its origin to the correlations of the electron motions in different atoms. The electrons of each atom shift with respect to the nucleus in the presence of other atoms and consequently an atom becomes an electric dipole. 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 derivation of the relevant expression for Φ^v can be understood from the fact that an electric field, of magnitude $(2\mu_1/r^3)$ is produced by the dipole moment of magnitude μ_1 of one atom at the center of the second atom at a distance r from the center of the first atom. This field in turn induces a dipole moment μ_2 on the second atom with a as electronic polarizability defined as dipole moment per unit electric field.

The potential energy due to these two dipole moments parallel to each other is given by

$$\Phi_{dd}^v(r) = -\frac{2\mu_1\mu_2}{r^3} = -\frac{4\alpha\mu_1^2}{r^6} = -\frac{c}{r^6} \dots (8)$$

This is known as VW dipole-dipole (d-d) interactions energy in which $c(=4\alpha\mu_1^2)$ is the VW coefficient.

According to the quantum theory of perturbation^{18,19}, vdW energy due to d-d interaction is expressed as:

$$\Phi_{dd}^v(r_{ij}) = -\frac{3}{2} \alpha_i \alpha_j \frac{E_i E_j}{E_i + E_j} \cdot \frac{1}{r_{ij}^6} = \frac{-c_{ij}}{r_{ij}^6} \dots (9)$$

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.

The VW coefficients c_{ij} have also been

evaluated from the Slater-Kirkwood variational method. Their relevant expressions obtained from this method are given by

$$C_{ij} = \frac{3}{2} \cdot \frac{e\hbar}{m^{1/2}} \cdot \frac{\alpha_i \alpha_j}{\left[(\alpha_i / N_i)^{1/2} + (\alpha_j / N_j)^{1/2} \right]^2} \dots (10)$$

Where m is the electronic mass, $\hbar = h/2\pi$ (h being the Planck's constant), α_i and N_i are the electronic polarizabilities and the number of effective electrons of i^{th} ion, respectively.

The total contributions due to d-d interactions are expressed as a sum of two-body interaction energies as:

$$\Phi^v(r) = \Phi_{dd}^v(r) = -\frac{C}{r^6} \dots (11)$$

Where C is the overall VWI coefficients. The Vdw coefficient c is defined as

$$C = -[S_v C_+ + \frac{1}{2} S_v (C_{++} + C_{--})] \dots (12)$$

C_+ can be determined by

$$C_+ = (C_{++} C_{--})^{1/2}$$

When S_v and S_v^{15} are respectively, lattice sums over unlike and like ions; C_+ , C_{++} , C_{--} ¹¹⁻¹⁵ are respectively, the Vdw coefficients for positive – negative, positive – positive and negative – negative ions.

Zero point energy

Further,

$$\text{Zero point energy} = \frac{1}{2} \sum_j \hbar \nu_0(j, q) \dots (13)$$

As reported by Seitz⁵ here h is Planck's constant and ν_0 is the zero point vibration frequency corresponding to the branch j and the phonon wave vector q .

Table 1:

Solids	Electro static or madelung energy (K cal/mol) [5]	Repulsive Energy (K cal/mol)[5]	Three body interaction energy (Kcal/mol present study)	Van der walls energy (Kcal/mol) (present study)	Zero point Energy (Kcal/mol) (present study)	Total cohesive energy (presnet study)		Experi- mental value of cohesive energy ¹⁷ (Kcal/mol)
						With vdW energy (Kcal/mol)	Without inclusion of vdW energy	
LiF	285.5	-44.1	15.74	8.00	-2.69	267.84	259.84	238.70
LiCl	223.5	-26.8	7.57	13.83	-1.41	219.47	205.67	195.30
LiBr	207.8	-22.5	7.44	16.53	-1.02	210.04	193.54	184.30
LiI	188.8	-18.3	3.23	20.53	-0.74	195.03	174.43	169.80
NaF	248.1	-35.3	5.12	11.12	-1.09	230.12	219.02	211.70
NaCl	204.3	-23.5	2.78	14.80	-1.27	199.68	184.88	179.50
NaBr	192.9	-20.6	1.70	16.61	-0.89	191.50	174.90	171.40
NaI	178.0	-17.1	-0.40	19.11	-0.67	180.30	161.20	160.20
KF	215.1	-28.1	-3.10	14.64	-1.41	200.00	185.30	185.60
KCl	183.2	-21.5	2.20	17.48	-1.01	182.40	164.90	160.70
KBr	174.5	-18.6	-1.20	18.98	-0.76	174.4	155.50	155.40
KI	162.8	-15.9	4.14	20.68	-0.59	172.34	151.64	146.30
RbF	203.8	-26.2	-3.45	15.74	-1.10	190.95	175.25	176.50
RbCl	175.8	-19.9	-4.37	18.30	-0.78	170.63	152.33	155.10
RbBr	167.2	-17.6	-2.00	19.62	-0.62	167.80	148.20	149.00
RbI	156.5	-15.4	-2.35	21.25	-0.50	160.25	139.25	140.60

ν_0 is the maximum frequency may be estimated to a sufficient degree of accuracy by using infrared absorption data or elastic data¹⁷. The concept of a centro-frequency, derived from the optical spectrum, has a mechanical analogy which may be derived from elastic (acoustic)

$$\text{spectrum as } \nu_0 = \frac{\sqrt{\frac{K}{\rho}}}{2r_0} \quad \dots(14)$$

Here r_0 is interionic distance is the density of solid & K is the Bulk modulus of alkali halides.

For present purpose, it is sufficiently accurate to use the Debye theory. According to which the frequencies are distributed between zero and a maximum ν_0 in the manner described by the density function.

$$f(\nu) = \frac{9N\nu^2}{\nu_0^3} \quad \dots(15)$$

Here, $f(\nu) d\nu$ is the no. of oscillators having frequencies in the range from ν to $\nu + d\nu$.

Thus, the total zero point energy for all range from 0 to ν_0 is

$$\int_0^{\nu_0} f(\nu_0) \frac{h\nu}{2} \cdot d\nu = \frac{9}{8} N h \nu_0 \quad \dots(16)$$

And the zero point energy per mole of a diatomic crystal is

$$E = \frac{9}{4} N h \nu_0 \quad \dots(17)$$

Thus the cohesive energy per mole is given by

$$\Phi = N\Phi(r) = N(\Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VWI}) + \frac{9}{4} N h \nu_0$$

Where,

$$\Phi^C(r_0) = - \left[\sum_{n_1, n_2, n_3}^{+\infty} \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \right] \cdot \frac{e^2}{r_0}$$

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

Table 2:

Solids	Cohesive Energy (K cal/mol) (Present Study)	Atomization energy [14] (Kcal/mol)
LiF	246.7	207.4
LiCl	209.1	170.8
LiBr	200.8	159.6
LiI	190.3	138.5
NaF	222.8	186.3
NaCl	194.3	161.8
NaBr	188.0	152.8
NaI	179.3	133.4
KF	200.2	182.8
KCl	178.2	163.5
KBr	174.1	157.0
KI	167.0	139.3
RbF	192.2	177.7
RbCl	173.4	161.9
RbBr	168.6	154.8
RbI	161.9	137.3

$$\Phi^{TBI} = e^2 \sum_{lk} \sum_{l'k'} \sum_{l''k''} Z_k f \left\{ (lk, l'k') \right\} \frac{Z_k''}{r(lk, l''k'')}$$

and

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

And N is Avogadro number.

Further the atomization energy (E_a) represented by

$$E_a = \Phi + E - I \quad \dots(18)$$

is considered to give better idea of stability of crystals than the cohesive energy, for alkali halides. Here E and I are the electron affinity of the anions and the ionization energy of cations, respectively⁷.

RESULT AND DISCUSSION

It is emergent from the descriptions that the most realistic model for the lattice dynamics and statics of these crystals can be developed by introducing the effect of van der Waals interactions (VWI), and three body interactions (TBI) in the framework of RSM, where the short-range

interactions have been considered up to the second neighbors. The development of such a lattice dynamical model has contributed extensively in the calculation of cohesive energies of alkali halides. The present model RSM in a way as outline above has been applied to investigate the complete cohesive energies of alkali halides. The effect of TBI and VWI and zero-point energies are quite significant and play a vital role in the description of cohesive energies of alkali halides. The atomization energies of alkali halides are compared with available theoretical calculation¹⁶ which gives satisfactory results.

The theoretical results thus obtained have been compared with experimental data^{5, 6,17} and found to show a reasonably good agreement. On the basis of its overall success our model RSM can be considered as a versatile model for the crystal dynamics of alkali halides.

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