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COMPUTATION OF COHESIVE ENERGY AND ALLIED ANHARMONIC PROPERTIES OF CHALCOGENIDES

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ABSTRACT: Cohesive energy and anharmonic properties such as Moelwyn – Hughes (C_1), Grüneisen parameter (γ), Anderson – Grüneisen parameter (δ), second Grüneisen – parameter (q) and Debye temperature (θ_D) have been computed for alkali earth oxides and Serenium BaO, CaO, MgO, SrO, BaSe, CaSe, MgSe and SrSe to ascertain the nearly true form of interionic interaction consisting of long range as well as short-range overlap repulsive interaction energy. The results so obtained are very close to the observed values. This study is capable enough to establish the relative superiority of one form of short-range interaction model over that of other model.

INTRODUCTION

The greatest challenge in the theory of solids is to account for the origin of the farces operative between the atoms in diatomic ionic crystals. The diatomic ionic crystals represent the simplest group of crystals composed of positive and negative ions arranged in a regular and periodic manner. The electronic configurations of these ions correspond to closed electronic shells as present in the inert gas atoms which have spherically symmetric charge distribution. The electrostatic interactions between the ions give rise to a net charge that binds the crystals together as each ion is preferentially surrounded by ions of opposite charges. In addition to electrostatic interaction, there exist repulsive forces acting between the negatively charged electron clouds to prevent the lattice from collapsing. These repulsive forces become appreciable whose the electron shells of neighbouring ions tend to overlap and they increase strongly in the region with decreasing values of interionic separation.

In the last few years several workers[1-11] have proposed and applied a number of empirical and semiempirical interaction potential model for ionic crystals in which the short-range part is either exponential function or logarithmic function or inverse power function. Of them inverse power function or logarithnie form have limited success. Exponential function has been found suitable to predict nearly all crystalline properties.

Theoretical Approach

In order to determine the exact form of short-range repulsive potential capable to produce the crystalline state properties, we have in our work adopted the generalized four terms potential due to Woodcock[12] in which the repulsive potential includes both an inverse power function due to Born-Lande[13] and exponential function due to Born-Mayer[14]. The proposed form of repulsive part is of the type

$$W_{ij}^{SR} = \frac{\beta_{ij} S}{\gamma_{ij}^{m}} \exp\left(-b_{ij}\, r_{ij}^{N}\right) \qquad (1)$$

Where i = positive ion
j = negative ion
and m = 1.75 and N = 1.30

The different ion-pair interactions have been incorporated to compute the effect of next nearest neighour (NNN). These ion-pair interactions are positive-negative ion-pair interaction $W_{ij}^{SR}(r)$, positive-negative ion pair interactions $W_{ii}^{SR}(r)$ and negative ion-pair interactions $W_{jj}^{SR}(r)$.

For diatomic ionic crystal interionic potential model (IPM) in general is expressed as such

$$W_L(r) = W_{LR}(r) + W_v + W_{TB} + W_{ij}^{SR}(r) \qquad (2)$$

Where W_{LR} is the long-range Coulomb interaction energy given as

$$W_{LR}(r) = -\frac{Az_1z_2e^2}{r} \qquad (3)$$

Here A is the Madelung constant

W_v = Van der Waals interaction energy expressed as

$$= -\frac{C}{r^6} - \frac{D}{r^8} \qquad (4)$$

Here C and D are vander Waals Co-efficients due to dipole-dipole and dipole quadrupole interaction terms. The three – body interactions energy W_{TB} is written as

$$W_{TB} = -\frac{nz_1z_2e^2}{r} f(r) \qquad (5)$$

This three body term arises from the charge transfer effect between adjacent ions and *f(r)* is TBI parameter dependent on the overlab integrals[15-16]

$$W_{SR}(r) = MS\beta_{ij}\, r_{ij}^{m}\, \exp\left[-b_{ij}\, r_{ij}^{N}\right] + \frac{M'S}{2}\left[\beta_{ii}\, r_{ii}^{-m} \exp\left(-b_{ii}r_{ii}^{N}\right) + \beta_{jj}r_{jj}^{-m} \exp\left(-b_{jj}r_{jj}^{N}\right)\right] \qquad (6)$$

Where M and M' are the number of nearest neighours (NN) and next nearest neighbour (NNN). *i* and *j* positive and negative ions respectively, β_{ij} is the Pauling's co-eeffecient given by

$$\beta_{ij} = 1 + \frac{Z_i}{N_i} + \frac{Z_j}{N_j} \qquad (7)$$

Where Z_i & Z_j are the valencies and N_i and N_j are number of outermost electrons of *i* and *j*

Calculations due to three-body interaction energy W_{TB} and $W_{ij}^{SR}(r)$ have been left out due to unavailability of useful input parameters in the literature in the case of BaSe, CaSe, MgSe, SrSe, BaO, CaO, MgO and SrO.

Table 1

Input parameters interionic equilibrium r_0, *vdw* constant C, D and hardness parameter ρ_{+-} and β_{+-}, β_{++}, β_{--}, b_{+-}, b_{++}, b_{--} are given table 1 and table 2 respectively.

Crystal	**r_0 (A°)**	ρ_{+-} (A°)	**C in 10^{-60} erg cm^6**	**D in 10^{-76} erg cm^8**
BaO	2.770	0.415	1046	2149
CaO	2.405	0.386	475	636
MgO	2.105	0.347	290	359
SrO	2.580	0.390	641	944

Table 2

Table 2 mentioned the evaluated values of hardness parameters $\beta_{+-}, \beta_{++}, \beta_{--}$ b_{+-}, b_{++} & b_{--} respectively.

Crystal	β_{+-}	β_{++}	β_{--}	b_{+-} **in 10^{10}**	b_{++} **in 10^{10}**	b_{--} **in 10^{10}**
BaO	1.0	1.5	0.5	1.60455	0.8022795	1.2836
CaO	1.0	1.5	0.5	1.76301	0.881506	1.41041
MgO	1.0	1.5	0.5	2.024840	1.0124204	1.6198726
SrO	1.0	1.5	0.5	-	-	-

Table 3

The values of *m*, *N*, K_1, *M*, M' and $Z_1 = Z_2 = Z = 2$ for BaO, CaO, MgO, SrO, are given in Table 3.

Crystal	**N**	***m***	**K_1**	***M***	M'	**$Z_1 = Z_2 = Z = 2$**
BaO	1.30	1.75	1.4142	6	12	2
CaO	1.30	1.75	1.4142	6	12	2
MgO	1.30	1.75	1.4142	6	12	2
SrO	1.30	1.75	1.4142	6	12	2

Table 4

Table 4 presents the interionic equilibrium r_0, *vwd* constant C and D are given in Table 4 for BaSe, CaSe, MgSe and SrSe

Crystal	**r_0 in A^0**	***C*- in 10^{-60} erg cm^{-N}**	***D*- in 10^{-76} erg cm^{-N}**	**$Z_1 = Z_2 = Z = 2$**
BaSe	3.300	2.486	5079	2
CaSe	2.955	1261	2549	2
MgSe	2.725	882	1536	2
SrSe	3.115	1624	3365	2

Table 5

W_{LR}(C) in K cal mol^{-1} W_V in K cal mol^{-1}. W in K cal mol^{-1}

Crystal	**W_{LR}(C) in K cal mol^{-1}**	**W_V in K cal mol^{-1}**	**W in K cal mol^{-1}**
BaO	-837.5675861	-42.2497	-879.81728
CaO	-964.6828	-43.49507	-1008.17787
MgO	-1102.167322	-60.632122	-1162.799444
SrO	-899.2489194	-38.2012066	-937.450121

Table 6

Values of Grüneisen parameter $(\gamma - \text{dimensionless})$ Anderson – Grüneisen parameter $(\delta - \text{dimensionless})$, Moelwyn – Hughes parameter (C_1) second Grüneisen – parameter $(q - \text{dimensionless})$ and Debye temperature $(\theta_D \text{ in } K)$.

Crystal	γ	δ	**C_1**	***q***	$(\theta_D \text{ in } K)$	
					Present Value[9-15]	**Calculated Value**
BaO	1.78	3.56	4.56	0.88	568.45	599
CaO	1.62	3.24	4.24	0.67	682.47	716
MgO	1.61	3.22	4.20	0.96	871.84	886
SrO	1.74	3.52	4.52	0.67	603.20	616

Table 7

Crystal	**W_{LR}(C) in K cal mol^{-1}**	**W_V in K cal mol^{-1}**	**W in K cal mol^{-1}**
BaSe	-703.0491556	-32.90217034	-735.9513203
CaSe	-785.1310369	-33.56887359	-818.6999103
MgSe	-851.3989776	-38.27399627	-889.6729757
SrSe	-744.803279	-31.04750833	-775.850787

Table 8

Values of Grüneisen parameter $(\gamma - \text{dimensionless})$ Anderson – Grüneisen parameter $(\delta - \text{dimensionless})$, Moelwyn – Hughes parameter (C_1) second Grüneisen – parameter $(q - \text{dimensionless})$ and Debye temperature $(\theta_D \text{ in } K)$.

Crystal	γ	δ	**C_1**	***q***	***q***	$(\theta_D \text{ in } K)$	
						Present Value[15-20]	**Calculated Value**
BaSe	1. 87	3.74	4.74	112	0.77	216.2	253
CaSe	1.82	3.64	4.70	2.32	1.34	324.06	385

MgSe	1.85	3.70	4.70	1.38	0.85	427.47	499
SrSe	1.93	3.86	4.86	1.14	0.78	253.12	294

Results and Discussion

The values of cohesive energy evaluated as sum of long-range coulomb interaction energy and van der Waals interaction energy terms for alkali earth oxides have been shown in Table 5.The results are in fairly good agreement with the observed values minor differences between the calculated and observed values may be due to the non-inclusion W_{TB} and W_{SR} interaction energy terms in the present values.

The anharmonic crystal behaviours for alkali earth oxides are expressed by Grüneisen, Anderson Grüneisen, Moelwyn- Hughes parameters are placed in Table 6.

Similarly, the values of cohesive energy and anharmonic properties for BaSe, CaSe, MgSe and SrSe have been shown in Table 7 and 8 respectively.

We expect that accuracy of the above calculation can be fully achieved if we are successful to include W_{TB} and W_{SR} by the calculation unknown and unavailable input second order elastic constant for above systems.

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