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THEORETICAL INVESTIGATION OF COHESION AND ANHARMONIC BEHAVIOUR OF SODIUM AND SILVER HALIDE CRYSTALS

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ABSTRACT: A rigorous theoretical approach has been employed to produce the cohesion and anharmonic behaviour of alkali (mainly sodium) and silver halide crystals evaluated by using the interaction potential model consisting of long range coulomb interaction vander Waals interaction (vdw) due to dipole-dipole and dipole-quadrupole interactions, three-body interactions (TBI) and a short-range overlap repulsive interaction operative up to the computation of next nearest neighbour (NNN). The values of coulomb energy, vander Waals interaction energy, overlap repulsive interaction energy, three-body interaction energy and hence the cohesive energy, isothermal bulk modules, Moelwyn hughes parameter, Debye temperature and Grüneisen parameter (using Slater, Dugdale Mc Donald and Free volume theories) have been computed and are very close to the observed values in literature.

Keywords:- Overlap short-range repulsive potential dipole-dipole dipole-quadruple interaction energy Moelwyn Hughes parameter, Grüneisen parameter etc.

INTRODUCTION

The study of harmonic as well as anharmonic behaviour of the crystal is of fundamental requirement to explain the interionic interaction that binds the atoms of the crystalline solid. The interaction potential model is a mathematical function based on classical electrostatic treatment of interionic interaction consisting of attractive and repulsive parts. The former (attractive) part is based on electrostatic interaction between oppositely charged ions separated by a distance while the latter is based on repulsive interaction between negatively charged electron clouds to prevent the lattice from collapsing. It has its origin from Pauli's principle.

In the last few years several workers1-11 have proposed and applied a number of empirical and semi-empirical interaction potential model (IPM) for ionic crystals in which the short-range repulsive part is either inverse power function or exponential function or logarithmic functions. Of them the inverse power function and the logarithmic have limited applications for ionic crystals and disfavored by some workers12. Only the exponential function has been found suitable to some extent for ionic crystals14.

Woodcock15 proposed a generalised potential in which repulsive potential includes both the inverse power function due to Born-Lande and exponential function due to Born-Mayer.

Nearly successful attempts16 (Singh & Khare) have been made to predict the cohesive energy of alkali halide. The form of SR repulsive potential employed was not fully capable enough of explaining all the observed macroscopic properties of ionic crystals. The search for potential model suitable to produce all the observed properties of ionic crystals, therefore, still continues.

Keeping in view all the requirements mentioned above, we have employed an interionic potential which consists of long range coulomb interaction (LR), Vander Waals dipole-dipole and dipole-quadrupole (q–d) interactions using Slater-Kirkwood variational method (SKV)17 and three-body interaction (TBI) found to play very important role in describing various static and dynamic properties of ionic solids18-21 and a complex form of short-range repulsive interaction (SRRI). The interaction proposed here has been used to calculate cohesive energy, isothermal bulk modules, Debye temperature, Moelwyn Hughes parameter and Grüneisen parameters.

Theoretical Analysis

The crystal energy of an ionic solid due to interaction between ions is expressed as

$$W = W_c + W_v + W_{TB} + W_{SR} \qquad (1)$$

The fort term W_c represents the long-range coulomb energy given by

$$W_c = -\frac{Az_1 z_2 e^2}{r} \qquad (2)$$

Where A is the madelung constant *r* is the separation between cation and anion. The second term W_v represents Vander interaction energy of the form

$$W_v = -\frac{C}{r^6} - \frac{D}{r^8} \qquad (3)$$

Where C and D are dipole-dipole and dipole-quadrupole Vander Waals co-efficient (W_{TB}) is three-body interaction energy and express as:

$$W_{TB} = -\frac{nz_1 z_2 e^2}{r} f\left(r\right) \qquad (4)$$

Here *n* is the constant dependent on the crystal structure. TBI arise from the charge transfer effect between the adjacent ions and *f*(*r*) is TBI interaction parameter dependent on overlap integral[19-20].

The last term is the short-range overlap repulsive energy which on taking consideration of the next nearest neighboring interaction assumes the form as

$$W_{SR} = MS\, B_{ij} r_{ji}^{-m} \ \exp\left(-b_{ij} r_{ij}^{N}\right) + \frac{M'S}{2}\Big[\beta_{00} \quad r_{vi}^{-m}$$
$$\exp\left(-b_{ii} r_{ii}^{N}\right) + \beta_{jj} r_{jj}^{-m} \exp\left(-b_{jj} r_{jj}^{N}\right)\Big] \quad (5)$$

Where M and M' are the number of NN and NNN for the given structures $r_{ii} = r_{ij} = 1.1547r$ fro CsCl structure and S is the repulsive strength parameter and b_{ij}, b_{ii} and b_{jj} are the repulsive hardness parameters to represent the cation-anion, cation-cation and anion-anion pair interactions.

β_{ij} is the Pauling's co-efficient given by

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \qquad (6)$$

Where Z_i and *Zj* are the valencies of *i* and *j* ions and n_i and n_j are the number of outermost electrons for cations and anions respectively.

Evaluation of potential parameters:

The repulsive strength parameter *S* or *P* is evaluated by applying crystal stability condition

$$\left(\frac{dw}{dr}\right)_{r=r_0} = 0 \qquad (7)$$

We obtain

$$\frac{S}{r_0^{\ 2}} = \frac{R}{P} \qquad (8)$$

where $R = 2\Big[\left\{Ae^2 r_0^{-1} + 6Cr_0^{-6} + 8Dr_0^{-8}\right\} + nAe^2 r_0^{-1}\left\{f(r_0) - r_0 f^1(r_0)\right\}\Big]$

(9)

and $P = M\beta_{+-} \exp\left(-b_{+-} r_0^{\ N}\right)\left(3b_{+-} r_0^{\ N} + 4\right)$

$$+\frac{M^1}{2K_1^{\ 2}}\Big\{\beta_{++} \exp\left(-b_{++} K_1^{\ N} r_0^{\ N}\right)\left(3b_{++} K_1^{\ N} r_0^{\ N} + 4\right)$$
$$+\beta_{--} \exp(-b_{--} K_1^{\ N} r_o^{\ N} (3b_{--} K_1^{\ N} r_o^{\ N} + 4\Big\} \ (10)$$

With $K_1 = 1.1547$

The values of r_0 used in the above calculation have been taken from Gate[12] and Mayer[2] While those of *C* and *D* from Vachaspati and R.P. Singh *et al.*[24]

The repulsive hardness parameters (b_{+-}, b_{++} and b_{--}) are evaluated using the relations

$$b_{+-} = \left(z_1 z_2\right)^p \left(\rho_{+-}^{-N}\right) \Big/ \left(K + 3.8\right) \qquad (11)$$

$$b_{++} = \left(b_{+-}\right) \Big/ k \qquad (12)$$

and $$b_{--} = \left(3b_{+-}\right) \Big/ \left(k + m\right) \qquad (13)$$

Where $p = 0.12$, $m = 2$, $N = 1.5$ and $k = 1.54$ for CsCl structure. The values of ρ_{+-} have been taken from Rana *et al*[25]. The three-body interaction (TBI) parameter $f(r)$ and its derivates have been computed using Cauchy relation[26] and Cochran relation[27].

For CsCl structure

$$C_{12} - C_{44} = 12.213 e^2 r_o^{-4} [r_0 f^1(r_o)]$$

For NaCl structure

$$C_{12} - C_{44} = 2.3301 \frac{e^2}{r_0^4} \left[r_0 f'\left(r_0\right)\right] \qquad (15)$$

and $$f(r) = fo(r) \exp(-r/\rho_{+-}) \qquad (16)$$

Where $f_o\,(r)$ is constant

The values of second order elastic constants (SOEC) used in the calculations are taken from Mayer[2] and Ladd, *et al*[23].

The isothermal bulk modulus (B_T), Moelwyn-Hughes parameter (C_1) and Debye temperature (θ_D) are computed with the help of following expressions.

$$B_T = r_o^{\,2} \frac{w''(r_0)}{9v} \qquad (17)$$

$$C_1 = \left(\frac{dB_T}{dp}\right) = 1 - \frac{r_0 w'''(r_o)}{3w''\left(r_o\right)} \qquad (18)$$

and $$\theta_D = \frac{h}{K_B}\left(\frac{5r_o B_T}{\mu}\right)^{\frac{1}{2}} \qquad (19)$$

Anharmonic Property:

Grüneisen parameter (γ) measures the anharmonicity of atomic vibration in crystals. The basic theory of γ was proposed by J.C. Slater[29] on the basis of theory of elasticity expressed as :

$$\gamma_5 = -1/6 + \frac{1}{2}\left(\frac{dB_T}{dp}\right) \qquad (20)$$

But Dugdale and Mc Donald[30] derived a general expression $\left(\gamma_{DM}\right)$ for γ given as:

$$\gamma_{DM} = -1/2 + \frac{1}{2}\left(\frac{dB_T}{dp}\right) \qquad (21)$$

In addition to these Vaschenko and Zubarov[31] developed a formulation of γ using free volume theory $\left(\gamma_{FV}\right)$ expressed as:

$$\gamma_{FV} = -5/6 + \frac{1}{2}\left(\frac{dB_T}{dp}\right) \qquad (22)$$

Results and Discussion:

The crystal cohesive energy *W* has been computed by using equation 1 and the results have been placed in Table 4. The results are found in good agreement with the experimental values available in scientific literature.

Values of input data for alkali and silver halides equilibrium interionic separation $\left(r_0 A^0\right)$, repulsive hardness parameter $\left(\rho_{+-}\ A^0\right)$ *vdw* constant *C* and *D* in 10^{-60} erg cm^6 and 10^{-76} erg cm^8 and elastic constants (SOEC) data $\left(C_{\alpha\beta} 10^{11} \text{dynes}\, cm^{-2}\right)$

Table 1

Crystal	**r_0 $\left(A^\circ\right)$**	ρ_{+-}	**C**	**D**	**C_{12}**	**C_{44}**
NaCl	2.820	0.306	492	180	2.280	2.460
NaBr	2.989	0.313	786	288	1.066	0.990
AgCl	2.7750	0.344	2113	952	3.620	0.925
AgBr	2.8874	0.366	2707	1212	3.3000	0.720

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

Table 2

Crystal	b_{+-}	b_{++}	b_{--}
NaCl	2.01898	1.00949	1.615191
NaBr	1.96048	0.980244	1.56839
AgCl	1.7339	0.8669	1.3891
AgBr	1.5997	0.7999	1.2798

Table 3 shows $\beta_{+-}, \beta_{++}, \beta_{--}, f(r_0)\quad f'(r_0)$ and $r_0 f'(r_0)$

Table 3

Crystal	β_{+-}	β_{++}	β_{--}	$f(r_0)$	$f'(r_0)$	$r_0 f'(r_0)$
NaCl	1.0	1.25	0.75	1.27709	-0.87826×10^{-6}	-1.7692×10^{-4}
NaBr	1.0	1.25	0.75	-11.82270	-4.223485×10^{-6}	-1.26239
AgCl	0.931	1.112	0.75	-0.02658	-10.71765×10^{-6}	-0.29613
AgBr	0.931	1.112	0.75	-0.03157	-11.55826×10^{-6}	-0.33217

Table 4 presents calculated value of W_{LR}, W_V, W_{TB}, W_{SR} and S. all in K.cal mol^{-1}

Table 4

Crystal	W_{LR}	W_V	W_{TB}	W_{SR}	W_S	$S\,\text{in}\,10^{-25}$
NaCl	-205.6792	-14.7278	0.15760	54.8865	-165.3629	3.4446
NaBr	-194.05003	-16.5141	1.37650	50.4356	-158.6064	3.9763
AgCl	-209.01550	-70.4936	33.3336	48.3333	-197.8422	2.0448
AgBr	-200.8	70.8433	-38.0503	29.3814	-204.8896	2.5781

Table 5 Shows Calculated value of μ, **isothermal bulk modulus** (B_T 10^{12} dyne cm^{-1}), Moelwyn-Hughes C_1 (dimensionless) α_v and Debye temperature θ_D in K.

Table 5

Crystal	μ	B_T	C_1	θ_D	$\alpha_v \times 10^{-5} K^{-1}$
NaCl	13.9474	0.2555	4.58	300.1	11.0
NaBr	17.8540	0.2250	4.70	250.94	11.9
AgCl	26.7177	0.414	5.40	273.6	97.7
AgBr	45.9374	0.359	5.36	198.1	104.5

Table 6 Shows the anharmonic properties γ_S, γ_{DM} and γ_{FV} all dimensionless

Table 6

Crystal	γ_S	γ_{DM}	γ_{FV}
NaCl	2.124	1.790	1.124
NaBr	2.184	1.8507	1.5174
AgCl	2.540	2.207	1.880
AgBr	2.514	2.1807	1.8474

The above results are in excellent agreement with the observed values fevered in literature.

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