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Effect of many body interactions on the isothermal bulk modulus of alkali halides

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ABSTRACT

The elastic shear stiffness constants of solids, correlated with other cohesive properties, provide a valuable insight into the nature of atomic binding forces. The deviations between calculated and measured values of isothermal bulk modulus of alkali halides have motivated us to frame a model for calculating the same for rock salt and cesium chloride 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 isothermal bulk modulus for all the alkali halides.

Key words: Alkali halides, Elastic shear stiffness constants, Isothermal bulk modulus.

INTRODUCTION

The study of isothermal bulk modulus alkali halides is very interesting, crystallizing into rock-salt structure except CsCl, CsBr and CsI, which has CsCl-structure. Although several theoretical models[1-7]. have been used to predict the isothermal bulk modulus or compressibility of these solids but only with moderate success. None of them is capable to explain the Cauchy violation ($C_{12} \neq C_{44}$), which is even larger value for CsCl-structure. Few proper applications of the Born-von Karman theory in the calculation of isothermal bulk modulus or Compressibility were suggested by the Woods *et al.* [8].

For better result Samunk 9., R.K. Singh and M.P. Verma[10]., Mohan and Sudha[11]., K.S.Upadhyaya *et.al.* [12-15], have employed three body force shell model which is a successful extension of the shell model and which includes the effect of electron shell displacement as well as deformations to study the lattice dynamics of sodium halides, Potassium halides and lithium halides, Rubidium halides, cesium halides and Uranium monochalcogenides. Although this approach is better than other but without including van der Waals interactions the complete elastic properties can not be investigated .The Cauchy relation ($C_{12} = C_{44}$), which is strongly violated by the experimental values of the elastic shear stiffness constants. In order to eliminate these draw backs from the two body potentials, one is compelled to incorporate the effect of many body interactions[16-18]., which take proper account of the Cauchy violation. In order to explain the isothermal bulk modulus of alkali halides better, we have employed a model which includes van der Waals interactions and three body interactions and short-range repulsion effective up to the second neighbors in the frame work of rigid shell model. Thus the isothermal bulk modulus of alkali halides has been investigated in terms of 12- parameters of van

derWaals three body shell model (vTSM).The vTSM theory used for description of lattice dynamics of alkali halides which will be published elsewhere, contains the 12-parameters. Out of which there six parameters for overlap repulsions (A_{11}, A_{22}, A_{12}, B_{11}, B_{22}, B_{12}),two for three body interactions (Z_m, r_of_o ') and four for electrical and mechanical polarizabilities(d_1, d_2, Y_1 and Y_2) .Here subscripts 1 and 2 refer to cations and anions,respectively. The knowledge of phonon dispersion relations is of fundamental importance for basic understanding to be gained of some physical properties such as thermal,elastic,dielectric and infrared properties. With the advent of the method of coherent neutron spectrometry, phonon dispersion relations have been obtained for most alkali halides crystals. he 12- parameters was determined by several researchers[31-34]. including our lattice dynamical groups[21-25]. from the available data of neutron scattering measurements[35] Since some of the vibration frequencies of zone-boundary points have been used to determine the model parameters,therefore,good agreement achieved for symmetry directions does not essentially guaranteed the agreement in the other general directions.

Theory

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 1933 16 The total potential for the alkali halides can be written as

$$\Phi = \Phi^{C} + \Phi^{R} + \Phi^{TBI} + \Phi^{VWI} \qquad ...(1)$$

When first term Φ^C is coulomb interaction potentials and is long-range in nature, second term is Φ^R short –range overlap repulsion potentials, third term Φ^{TBI} is three-body interaction potentials and the last term is Φ^{VWI} van der Waals interaction potentials and owes its origin to the correlations of the electron motions in different atoms. We consider that van der Waals energy converges fast but the overlap repulsion converges much faster. Therefore, the overlap repulsion is effective only up to the first neighbors and the van der Waals attractions up to the second neighbors[17]. This means that the second neighbors forces are entirely due to van der Waals interactions and the first neighbor forces are the results of the overlap repulsion and the van der Waals attractions between the nearest neighbors. Therefore,

...(2)

The various potentials are described in detail by Aziz *et.al*[36].

Using the crystal potential expression (2.1) the equations of motion of two cores and two shells can be written as

$$\omega^2 \underline{M}\underline{U} = (\underline{R} + \underline{Z_m}\underline{C}'\underline{Z_m})\underline{U} + (\underline{T} + \underline{Z_m}\underline{C}'\underline{Y_m})\underline{W} \quad ...(3)$$

...(4)

Here U and W are vectors describing the ionic displacements and deformations, respectively. Z_m and Y_m are diagonal matrices of modified ionic charges and shell charges, respectively. The elements of matrix S consists of the parameter Z_m giving the modified ionic charge.

$$Z_m = Z\xi = \pm Z\sqrt{1+(n/Z)f0} \qquad ...(5)$$

This means that the ionic charge parameter (Z) of RSM gets modified by a factor $\{1+(12/Z)f_0\}$ for NaCl – structure and $\{1+(16/Z)f_0\}$ for CsCl -structure in vTSM.

However, the core and shell charge parameters (X, Y) of RSM will be modified to (Xξ, Yξ). These modifications lead to the following relation.

$$Z_m = Z\xi = X\xi + Y\xi \qquad ...(6)$$

Such that X+Y=Z; R, T and S are matrices describing various short-range interactions in the crystal. C' is the modified long-range interaction matrix given by

$$C' = C + (Z_m^{-2} Z r_0 f_0')V + (Z^2 Z_m^{-2})D \qquad ...(7)$$

Here D is a matrix contributed by the van der Waals interactions.

The elimination of W from equations (2.3) and (2.4) leads to the secular determinant:

...(8)

Here D (q) is the (6×6) dynamical matrix given by

$$\underline{D}\vec{q} = (\underline{R}' + \underline{Z_m}\underline{C}'\underline{Z_m}) - (\underline{T} + \underline{Z_m}\underline{C}'\underline{Y_m}) \times (\underline{S} + \underline{K} + \underline{Y_m C}'\underline{Y_m})^{-1}(\underline{T}^T + \underline{Y}_m\underline{C}'\underline{Z}_m) \quad ...(9)$$

Elastic Properties of NaCl- like structure

In the long wavelength limit (as $\vec{q} \to 0$) the acoustic vibration frequencies tends to zero in such a way that $(\omega/q)^2$ attain definite limits. A solution of (2´2) secular equation (2.8) for an acoustic vibration frequency (w) leads to the first non-vanishing term in the expression of w^2 which contains a multiplicative factor q^2. This term, when subjected to attains a finite limit which is related to the elastic constants (C_{11}, C_{12}, C_{44}) such that

...(10)

Where *D* (11). $_2$ ..... etc. are the coefficients of $(-q^2)$ in the expression of $D_{\alpha\beta}\left(\vec{q}_{kk'}\right)$ expressed in powers of . The expressions derived for elastic shear stiffness constants from equation (2.8) corresponding to vTSM is obtained as

...(11)

$$\frac{4r_0^4}{e^2}C_{12} = [0.226Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22} + 5B_{11} + 5B_{22}) + 9.3204\xi'^2]$$

...(12)

$$\frac{4r_0^4}{e^2}C_{44} = [2.556Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22} + 3B_{11} + 3B_{22})]$$

...(13)

In view of the equilibrium condition $(d\Phi/dr)_0 = 0.$, we obtain

$$B_{11} + B_{12} + B_{22} = -1.165Z_m^2 \quad ...(14)$$

Where,

$$Z_m = \pm Z\sqrt{\left\{1 + \frac{12\,f(r)}{Z}\right\}_0}$$

and

...(15)

The term $f(r)$ is a function dependent on the overlap integrals of the electron wave functions and the subscript zero on the brackets indicates the equilibrium values of the quantities inside.

Elastic properties of CsCl- like structure

$$C_{11} = \frac{e^2}{4a^2}\left[10.7010Z_m\frac{A_{12}+2B_{12}}{6} + \frac{A_{11}+A_{22}}{4} + 5.4283\xi^2\right]$$

...(16)

$$= \frac{4\pi^2}{\rho}(\text{linear combination of } C_{ij})$$

...(17)

...(18)

In view of the equilibrium condition ($[d\Phi/dr)_0$=0. we obtain

...(19)

Where

$$Z_m^2 = Z^2\left(1 + \frac{16}{Z}f_0\right) \text{ and } \quad \xi^2 = Zr_0 f'_0 \quad ...(20)$$

$f'_0(df/dr)_{r=r0}, r_0 = a\sqrt{3}$ is the interionic separation.

The term f_0 is a function dependent on the overlap integrals of the electron wave functions and the subscript zero indicates the equilibrium value.

(A_{12}, B_{12}) and (A_{11}, A_{22}, B_{11}, B_{22}) are the short-range parameters for the nearest neighbors and the next nearest neighbors, respectively. These are defined by

$$B_{12} = \frac{4r_0^2}{e^2}\left[\frac{d}{dr}\Phi_1^{(R)}(r)\right]_{r=r_0}, A_{12} = \frac{4r_0^3}{e^2}\left[\frac{d^2}{dr^2}\Phi_1^{(R)}(r)\right]_{r=r_0} \quad ...(21)$$

$$\sqrt{2}(A_{11}+A_{22}) = \frac{4\left(r_0\sqrt{2}\right)^3}{e^2}\left[\frac{d^2}{dr^2}\Phi_2^{(R)}(r)\right]_{r=r_0\sqrt{2}} \quad ...(22)$$

Where, $\Phi_1^{(R)}(r)$ and $\Phi_2^{(R)}(r)$ are the overlap potentials between the nearest neighbors and the next nearest neighbors, respectively.

The modified expressions for the electrical and mechanical polarizabilities are defined by the following relations:

$$a_i = \frac{\left(Y_i Z_m\right)^2 e^2}{R_0 + K_i}, \qquad (i = 1,2) \quad ...(23)$$

and

$$d_i = \frac{-R_0\left(Y_i Z_m\right)}{R_0 + K_i} = -\frac{a_i R_0}{Ze^2\left(Y_i Z_m\right)} \quad (i = 1,2)$$

$$R_0 = \frac{Z^2 e^2}{V} = (A_{12} + 2B_{12}) \quad ...(24)$$

The SOE constants lead to the Cauchy violation,

$$C_{12} - C_{44} = \frac{e^2}{4r_0^4}[9.3304 Z r_0 f_0'] \quad ...(25)$$

For NaCl-like structure

$$C_{12} - C_{44} = \frac{e^2}{4a^2}[5.4383 Z r_0 f_0'] \quad ...(26)$$

For CsCl-like structure

Where r_o (= $a\sqrt{3}$), is the interionic distance. The isothermal bulk modulus or the compressibility (β) is define by

$$K = \frac{1}{\beta} = \frac{C_{11} + 2C_{12}}{3} \quad ...(27)$$

The derivation implies that these formulae are true for the static lattice only.

EXPERIMENTAL

Support for above theory

It can be seen from equation (2.8) that the acoustic modes of long wavelength ($q \to 0$) propagate as in continuous medium and their frequencies, acoustical and polarization properties are related to the elastic constant of the crystal. The most accurate method to measure the second-order elastic constant (SOEC) in the ultrasonic pulse echo technique in which an ultrasonic pulse (of frequencies 10-^{17} sec^{-1}) generated by a quartz transducer is injected into a block of crystal (of length 1cm.) and reflected from its surface to the transducer. The time taken between initiation and reception of the pulse is measured by standard electronic methods. If the waves are longitudinally polarized and the direction is 100. in a cubic crystal, C_{11} can be immediately determined. The remaining elastic shear stiffness constants (C_{12} and C_{44}) can be measured from the velocities of longitudinal and of transverse waves traveling in other directions 110. and 111 The details of the technique of measuring SOEC and their values thus determined have been reported 19, 20

$$K = \frac{1}{\beta} \simeq \frac{C_{11} + 2C_{12}}{3} = \frac{4\left(r_0\sqrt{2}\right)^3}{3\sqrt{2}(B_{11} + B_{22})}\left[\frac{d^2}{dr^2}\Phi_2^{(R)}(r)\right]_{r=r_0\sqrt{2}}$$

Computation

Calculated values of isothermal bulk modulus and its comparison with experimental data[26,27].

RESULTS AND DISCUSSION

Having taken, the van der Waals interactions and three body interactions in the frame work of rigid shell model, we have calculated the values of isothermal bulk modulus for alkali halides crystals. The calculated values of bulk modulus have close agreement with the experimental value[26, 27] The only limitation of the model is requirement of

Table 1:

Solids	Structure	Elastic shear stiffness constnat c_{11} (10^{11}dyne/cm²)	Elastic shear stiffness constnat c_{12} (10^{11}dyne/cm²)	Elastic shear stiffness constnat c_{44} (10^{11}dyne/cm²)	Bulk modulus (10^{12} dyne/cm²) obtained from equation (2.22) (present study)	Experimental value of Bulk modulus(10^{12} dyne/cm²) [26,27]
LiF	NaCl	11.866	4.340	6.590	0.684	0.674
LiCl	NaCl	5.974	2.270	2.492	0.350	0.300
LiBr	NaCl	4.731	1.890	2.652	0.284	0.238
LiI	NaCl	3.107	1.431	1.467	0.199	0.175
NaF	NaCl	9.760	2.330	2.890	0.480	0.471
NaCl	NaCl	4.986	1.230	1.285	0.248	0.240
NaBr	NaCl	4.812	0.990	1.090	0.226	0.197
NaI	NaCl	3.026	0.890	0.780	0.160	0.151
KF	NaCl	7.576	1.450	1.326	0.349	0.306
KCl	NaCl	4.098	0.642	0.662	0.179	0.176
KBr	NaCl	3.986	0.560	0.521	0.170	0.148
KI	NaCl	3.480	0.320	0.368	0.137	0.117
RbF	NaCl	5.850	1.135	0.945	0.271	0.271
RbCl	NaCl	4.398	0.616	0.489	0.188	0.158
RbBr	NaCl	3.163	0.494	0.388	0.138	0.134
RbI	NaCl	3.090	0.360	0.282	0.127	0.106
CsF	NaCl	-	-	-	-	0.235
CsCl	CsCl	4.168	1.300	1.106	0.226	0.180
CsBr	CsCl	3.299	1.102	0.862	0.183	0.159
CsI	CsCl	3.004	0.826	0.596	0.155	0.128

the knowledge of certain experimental information to be used as input data. It is evident from the above results that second neighbor interactions (SNI) do not affect the Cauchy violations but they strongly influence the compressibility and hence the isothermal bulk modulus of solids.

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