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VOLUME DEPENDENCE STUDY OF GRUNEISEN PARAMETER IN ALKALI HALIDES

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ABSTRACT

The Gruneisen parameter and its volume dependence in NaCl structure alkali halides are evaluated considering appropriate models for interionic potentials. The potential parameters are derived from the recent data measured. Gruneisen parameter and its volume dependence are found to present good agreement with experimental data. In the present study we adopt four interionic force models. In model I we consider the long range electrostatic forces to be balanced by the short range repulsive interactions operative between nearest neighbors only. In Model II we have also included the van-der-waals dipole-dipole and dipole-quadrupole interaction energies as are important in the development of an adequate interatomic force model for alkali halides ***[11]****,* ***[4]*** *and* ***[19]****.*

INTRODUCTION:

Recent studies on the cohesive elastic, dielectric and lattice dynamical properties of ionic solids have clearly revealed the importance of van-der-waals (vdw) potentials, particularly emphasizing the fact that the magnitude of these potentials is significantly larger than those calculated by **[20]**. A theoretical method based on interionic potentials is developed for evaluating the compression of alkali halide crystals corresponding to different values of pressure.

To investigate the enharmonic or nonlinear behaviour of ionic crystals it is necessary to evaluate the pressure or volume derivatives of dielectric constants. Similarly an analysis of higher order elastic constants is needed to evaluate the vibrational contributions containing coupling parameters of higher order which are directly related to the harmonic behaviour. Thus the pressure derivatives of dielectric constants as well as higher order elastic constants are directly related to harmonic effects in crystals. Expressions for the third order elastic constants (TOEC) and the first order pressure derivatives of the second order elastic constants (SOEC) of rare gas solids are derived from a many body potential proposed elsewhere.

The knowledge of third and higher order elastic constants is important for the study of the harmonic behaviour of solids. The third order elastic constants (TOEC) and the fourth order elastic constants can be obtained as functions of the derivatives of sound velocities with respect to applied pressure or uniaxial stress which in turn can be directly derived from the crystal potential. The studies on volume and pressure derivatives of dielectric constants of ionic crystals are useful to make a critical test of the theories of dielectric polarization and interionic forces operative in these crystals. Measurements of first, second and third order pressure derivatives of static or low frequency dielectric constant have been performed for a number of ionic crystals **[18], [1]** .

The temperature dependence of dielectric constants is directly related to the anharmonic properties. The Gruneisen parameter and its volume dependence in NaCl structure alkali halides are evaluated considering appropriate models for interionic potentials. Effect of including the next nearest neighbour interactions, Van-der-waals potentials and three body forces has been investigated. The potential parameters are derived from the recent data measured ultrasonically. Various properties of crystalline materials can be calculated accurately provided the interatomic forces in these materials are known adequately.

I have to develop a simple ab initio model for the calculation of the thermoelastic properties of ionic compounds. The model is based on the Gordon-Kim-type electron-gas theory with spherically symmetric relaxation of ionic charge densities. The relaxation is controlled by a spherically averaged potential due to the total crystal charge density. I have on hope that these potential yields anion that are slightly smaller than those stabilized by a point ion coulomb potential only.

THEORY

An expression for the Gruneisen parameter which is valid at all pressures has been obtained by DM as follows:

$$\gamma = -1 - \frac{v}{2}\left(\frac{\partial^2 P}{\partial^2 V^2} - \frac{10P}{9V^2}\right)\left(\frac{\partial P}{\partial V} - \frac{2P}{3V}\right)^{-1} \qquad (1)$$

The volume derivative of γderived from eqn. (1) given by

$$q_0 = -\frac{v}{2\gamma}\left[\left(\frac{\partial^2 P}{\partial V^2}\right)\left(\frac{\partial P}{\partial V}\right)^{-1} + V\left(\frac{\partial P}{\partial V}\right)^{-1}\left(\frac{\partial^3 P}{\partial V^3} - \frac{10}{V^2}\frac{\partial P}{\partial V}\right)\right.$$

$$\left. - V\left(\frac{\partial^2 P}{\partial V^2}\right)\left(\frac{\partial P}{\partial V}\right)^{-2}\left(\frac{\partial^2 P}{\partial V^2} + \frac{2}{3V}\frac{\partial P}{\partial V}\right)\right] \qquad (2)$$

where q_0 is the value of q at p=0

Model-1

In this model we consider that the long range electrostatic forces are balanced by the short range overlap repulsive forces acting between nearest neighbours only. Thus the crystal lattice energy is given by

$$W = -\frac{\alpha_m e^2}{r} + Mb\,\beta +- \exp\left(\frac{r_+ + r_- - r}{\rho}\right) \qquad (3)$$

Model-II

In this model we also consider the van-der-waals dipole dipole and dipole quadrupole interactions. The crystal potential energy is now expressed as

$$W = -\frac{\alpha_m e^2}{r} + Mb\,\beta\; + - \exp\left(\frac{r_+ + r_- - r}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^B} \qquad (4)$$

Where C and D are the dipole-dipole and dipole-quadrupole coefficients.

Model-III

In this model the van-der-waals interactions as well as the second neighbour repulsive interactions have been taken into account within the framework of this model the crystal potential energy is written as

$$W = -\frac{\alpha_m e^2}{r} + Mb\,\beta_{+-}\; \exp\left(\frac{r_+ + r_- - r}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^B}$$

$$+\frac{1}{2}M'b\,\beta_{++}\; \exp\left(\frac{2r_+ - \sqrt{2r}}{\rho}\right) + \frac{1}{2}M'b\beta\exp\left(\frac{2r_+ - \sqrt{2r}}{\rho}\right) \qquad (5)$$

where M' is the number of next nearest neighbours, $\sqrt{2r}$ is the distance between second neighbours.

Model-IV

In this model we also take account of the effect of three body potential arising from the overlap of ions **[3]** . The consideration of three body potential modifies the long range as well as short range interactions lattice energy within the framework of this model is written as

$$W = -\frac{\alpha_m (Z'e)^2}{r} + Mb\,\beta_{+-}\; \exp\left(\frac{r_+ + r_- - r}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^B}$$

$$+1M'b + \beta_{++}\; \exp\left(\frac{2r_+ - \sqrt{2r}}{\rho}\right) + \frac{1}{2}M;b\,\beta_{--}\; \exp\left(\frac{2r_- - \sqrt{2r}}{\rho}\right) \qquad (6)$$

where Z' e is the modified charge on the ions while for NaCl type crystals.

ANALYSIS AND RESULTS:

Values of w^I, w^{II}, w^{III} and w^{IV} estimated from different models are obtain the Gruneisen parameter γ and its volume dependence $v_0 = \frac{\partial I_n \gamma}{\partial I_n V}$. The new ultrasonic data which have been used in the present study provide a better understanding of interionic forces in alkali halides **[10]** . In calculating the potential parameters we have taken the ionic radii from **[9]** . The calculated values of the potential parameters are given in Table 1.

Table-1

Crystal	**Model- I b** **$\rho(A^0)10^{-12}$ erg**		**Model-II b** **$\rho(A^0)10^{-12}$ erg**		**Model-III** **b 10^{-12}erg**	**Model-IV** **b 10^{-12}erg**	**F**
LiF	0.270	0.264	0.270	0.269	0.251	0.304	0.0021
LiCl	0.290	0.197	0.291	0.208	0.185	0.275	0.0039
LiBr	0.294	0.184	0.299	0.208	0.178	0.301	0.0055
Lil	0.299	0.163	0.308	0.191	0.151	0.328	0.0087
NaF	0.267	0.318	0.269	0.342	0.315	0.407	0.0025
CaCl	0.286	0.216	0.296	0.258	0.233	0.332	0.0035
NaBr	0.287	0.196	0.308	0.271	0.236	0.381	0.0055
Nal	0.296	0.175	0.316	0.232	0.187	0.391	0.0086
KF	0.269	0.270	0.281	0.340	0.298	0.461	0.0047
KCl	0.287	0.176	0.309	0.240	0.231	0.268	0.0014
KBr	0.297	0.160	0.329	0.245	0.233	0.283	0.0020
Kl	0.305	0.140	0.344	0.223	0.208	0.276	0.0030
RbF	0.263	0.247	0.289	0.271	0.308	0.537	0.0070
RbCl	0.284	0.160	0.311	0.231	0.223	0.257	0.0013
RbBr	0.292	0.146	0.322	0.213	0.207	0.236	0.0012
RbI	0.299	0.124	0.346	0.214	0.206	0.246	0.0019

A comparison of the calculated values of γ with thermodynamic values is presented in Table 2. Values of γ can also be determined from Change's relation **[5]** .

Crystal	**Model- I**	**Calculated**			Based on experimental data	
		Model- II	**Model- III**	**Model- IV**	(a)	(b)
LiF	1.57	1.56	1.68	1.54	1.63	2.15
LiCl	1.83	1.83	2.06	1.82	1.81	2.31
LiBr	1.94	1.91	2.23	1.91	1.94	2.34
Lil	2.09	2.05	2.54	2.00	2.19	2.57
NaF	1.79	1.77	1.93	1.78	1.51	2.12
CaCl	2.01	1.97	2.19	1.97	1.61	2.19
NaBr	2.12	2.02	2.35	2.02	1.64	2.22
Nal	2.22	2.13	2.63	2.09	1.71	2.29
KF	2.02	1.96	2.24	1.95	1.52	2.19
KCl	2.20	2.11	2.21	2.12	1.49	2.23
KBr	2.24	2.10	2.24	2.11	1.50	2.23
Kl	2.32	2.16	2.36	2.17	2.53	2.28
RbF	2.15	2.03	2.43	2.02	1.40	2.34
RbCl	2.31	2.19	2.28	2.19	2.39	2.31
RbBr	2.35	2.22	2.31	2.23	1.42	2.29
RbI	2.45	2.24	2.37	2.23	1.56	2.30

(a) **[10]**

(b) **[5]**

$$\gamma = \frac{1}{2}\left(\frac{dB_\tau}{dP} - 1\right) \tag{7}$$

The experimental values of $\frac{dB_\tau}{dP}$ have been reported by**[6],[7]** and **[8]** . Values of γ based on eqn. (7) are included in Table 2. It is seen from there that the agreement between theory and experimental is good.

CONCLUSION:

We have performed an analysis of the Gruneisen parameter and its volume dependence for NaCl structure alkali halides within the framework of the DM theory using appropriate interionic force models. The results obtained from these interionic models are found to be consistent with previous investigations. The appropriateness of the interaction models can be demonstrated by calculating the crystal energies and comparing the results with experimental data.

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