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## Analysis of crystalline state properties of chalcogenide crystals with antiferroelectric structure

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### ABSTRACT

Hellmann and Ali-Hasan forms of repulsive potential functions have been applied to compute the values of cohesive energy, force constant, I.R. absorption frequency, Debye temperature, Gruneisen parameter, Anderson Gruneisen parameter and Moelwyn-Hughes parameter for 14 chalcogenide crystals of antiferroelectric structure are reported. Calculations are also performed for the estimation of first order volume dependence of Gruneisen parameter commonly known as second Gruneisen parameter using expressions of higher order derivatives of interaction potential within the framework of Dugdale and Mac Donald theory. The high pressure behaviour of these crystals have also been studied. The results obtained here may add a little to the physics and chemistry of these crystals it may be useful for experimentalists also. © 2009 Trade Science Inc. - INDIA

### KEYWORDS

Crystalline state properties;  
Gruneisen parameter;  
Second gruneisen parameter.

### INTRODUCTION

The nature of bonding in ionic crystals has been the centre of attraction for theoretical as well as experimental physicists and chemists as it plays a vital role in solid state physics. Several attempts have been made to understand the nature of interaction between the atoms of an ionic crystal and hence to decide the form of interaction potential for such a crystal. Once the reliable form of interaction potential is known, it is possible to study the crystalline state properties of chalcogenide crystal. The crystal state properties of chalcogenides have been studied by several workers. But these investigators employed the interaction models<sup>[1-4]</sup> with repulsive parts that are either inverse power functions or exponential functions or phenomenological in nature.

But none of these are capable enough of explaining all the observed macroscopic properties of diatomic crystals. The search for the interaction potential function satisfying the essential requirements of ideal potential function<sup>[5]</sup> continues. The chalcogenides of Li, Na, K and Rb are suitable host crystals for transition metal ions and rare earth ions<sup>[6]</sup>. A knowledge of interionic potentials in host crystals is of considerable value. The alkali chalcogenides which crystallize in antiferroelectric structure are relatively unexplored.

In the present paper we have used the Hellmann<sup>[7]</sup> and Ali-Hasan<sup>[8]</sup> short-range repulsive potential to evaluate the crystalline state properties of chalcogenide crystals. The reason for selecting these models lies in their suitability<sup>[9]</sup> of evaluating their state properties as well as molecular state properties. Moreover, these

potentials fulfill the fundamental physical requirements of an ideal potential.

### Method of analysis

#### Crystal energy :

The crystal lattice energy per ion pair can be expressed as

$$\Phi(r) = \Phi_c + \Phi_v + \Phi_{SR} \quad (1)$$

Here  $\Phi_c$  is the long-range electrostatic coulomb energy with Madelung constant A. it is given by

$$\Phi_c = -Az_1 z_2 e^2/r \quad (2)$$

Where  $z_1 e$  and  $z_2 e$  are the electrostatic charges on the ion pairs and  $r$  is the interionic separation.

The second term,  $\Phi_v$ , on the R.H.S. of the eq (1) represents the van der Waals energy expressed as

$$\Phi_v = -C/r^6 - D/r^8 \quad (3)$$

Where C and D are van der Waals (vdw) dipole-dipole and dipole quadrupole co-efficients and are given by

$$C = S_{+-} c_{+-} + S_{++} c_{++} + S_{--} c_{--} \\ \text{And } D = T_{+-} d_{+-} + T_{++} d_{++} + T_{--} d_{--} \quad (4)$$

Lattice sums  $S_{ij}$  and  $T_{ij}$  have been taken from Tosi<sup>[10]</sup> and vdw co-efficients  $c_{ij}$  and  $d_{ij}$  are taken from Shankar, Singh and Agarwal<sup>[11]</sup>.

The last term  $\Phi_{SR}$  on the R.H.S. equation (1) is expressed as

$$\Phi_{SR} = S/r^m \exp(-\lambda r^n) \quad (5)$$

Where S and  $\lambda$  are potential parameters evaluated by applying the following crystal stability conditions :

$$\Phi'(r_0) = 0 \\ \text{and } \Phi''(r_0) = 9kr_0/\beta \quad (6)$$

Where  $k$  = crystals structure constant, and  $\beta$  = isothermal compressibility

In the above equations  $r_0$  is the equilibrium interionic separation in the lattice and the primes denote derivatives with respect to  $r$ .

The application of the above conditions to the potentials function yields the expression for the potential parameters :

$$S = \frac{r^m [Az_1 z_2 e^2/r_0 + 6C/r_0^6 + 8D/r_0^8]}{\exp(-\lambda r_0^n) (m + n\lambda r_0^n)} \quad (7)$$

and

$$\lambda = \frac{X + n - 2m + 1 + [(X + n - 2m - 1)^2 + 4m(M + 1)] X^{1/2}}{r_0^n 2n} \quad (8)$$

where

$$X = \frac{9kr_0^3 + 2Az_1 z_2 e^2/r_0 + 42C/r_0^6 + 72D/r_0^8}{Az_1 z_2 e^2/r_0 + 6C/r_0^6 + 8D/r_0^8} \quad (9)$$

Where  $z_1 = 2$  and  $z_2 = 1$ , for Alkali Chalcogenide crystals and  $m = 1$ ,  $n = 1$ , for Helmann potential,  $m = 2$ ,  $n = 3/2$ , for Ali-Hasan model

The last term  $\Phi_{SR}$  eq. (1) is the short-range overlap repulsive energy dominant in diatomic crystals. The short-range repulsive potential perturbs the spherically symmetric closed shell of an ion in a lattice as the ions are brought closer so that outer electron shells began to overlap. An additional characteristic repulsive force becomes operative resulting from the overlapping of the ions. This repulsive force opposes the Coulombian attractive force operating between the positive and the negative ions and causes them to come to equilibrium at finite value of the interionic distance ( $r_0$ ). This repulsive force in an ion becomes dominant at a very short distance, so it is known as short-range repulsive potential (SRRP). The exact form of SRRP in literature is still lacking.

#### Cohesive energy

The cohesive energy  $W$  per mole is related to the interaction potential energy function  $\Phi(r)$  by

$$W = -N \Phi(r) \quad (10)$$

Where  $N$  is Avogadro's number

#### Force constant (f), IR absorption frequency ( $\nu_0$ ) and Debye temperature ( $\theta_D$ )

The force constant  $f$  is defined<sup>[12]</sup> as

$$F = 1/3[\Psi''(r_0) + 2r_0^{-1} \Psi'''(r_0)] \quad (11)$$

Where  $\Psi(r)$  is the non-Coulombic part of  $\Phi(r)$  and  $r_0$  is the equilibrium interionic distance in crystalline states.

The IR absorption frequency ( $\nu_0$ ) is given<sup>[12]</sup> by

$$\nu_0 = 1/2\pi(f/m)^{1/2}$$

Where  $m$  is the reduced mass.

Once the value of  $\nu_0$  is obtained, the Debye temperature  $\theta_D$  can be calculated from the relation,

$$\theta_D = h \nu_0/k$$

Where  $h$  is the Planck's constant and  $k$  is the Boltzmann constant.

#### Gruneisen parameter, anderson-Gruneisen parameter and moelwyn-hughes parameter

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The Gruneisen parameter  $\gamma$  is the first significant measure of the anharmonicity in solids. It is related to  $\Phi(r)$  by [12]

$$\gamma = (-1/6)r_0 \Phi''(r_0)/\Phi''(r_0) \quad (12)$$

Where  $\Phi''(r)$  and  $\Phi'''(r)$  refer to the second and third derivatives of  $\Phi(r)$ .

### The anderson-Gruneisen parameter

Anderson-Gruneisen Parameters  $\delta$  have been computed using chang's expression [13] connecting  $\gamma$  and  $\delta$  which was derived on the basis of Dugdale and Macdonald formula [14] relating  $\gamma$  to the change of compressibility with volume.

The values of the Moelwyn-Hughes parameter  $C_1$  have been computed for the potential  $\Phi(r)$  using the relation [12]

$$C_1 = 1 - (r_0^3 \beta / 27V) \Phi'''(r_0) \quad (13)$$

Where  $\beta$  is the compressibility of the crystals.

### Second gruneisen parameter

The first order volume dependence of the Gruneisen parameter commonly known as the second Gruneisen parameter is fundamental to the study of many basic phenomena in solids. It is an additional measure of the anharmonicity in solids.  $\gamma$  and  $q$  can be used to make predictions of a variety of physical properties such as the equation of state of a material and are related to thermodynamic properties. These are also important in the study of thermo-elastic properties in terms of shock-waves. The latter property is especially relevant to the study of the geophysics of the earth.

In general, the Gruneisen parameter is a function of both temperature and volume. The temperature of Gruneisen parameter for a large number of diatomic crystals can be fairly determined either experimentally or theoretically.

In this communication an attempt has been made to calculate  $q$  for chalcogenide crystals using Hellman and Ali-Hasan forms of interaction models within the frame work of Dugdale and Macdonald theory (DM).

Gruneisen parameter ( $\gamma$ ) based on DM theory valid at all pressures may be expressed as

$$\gamma = -1 - V/2 (\partial^2 P / \partial V^2 - 10P/9V^2) (\partial P / \partial V + 2P/3V)^{-1} \quad (14)$$

The second Gruneisen parameter ( $q$ ) derived from eq (1) is written as [15]

$$q = -V/2\gamma [(\partial^2 P / \partial V^2 - 10P/9V^2) (\partial P / \partial V + 2P/3V)^{-1} + (\partial P / \partial V + 2P/3V) (\partial^3 P / \partial V^3 - 10/V^2 \partial P / \partial V + 20P/V^3) - V(\partial^2 P / \partial V^2 - 10P/9V^2) (\partial P / \partial V + 2P/3V)^{-2} (\partial^2 P / \partial V^2 + 2/3V \partial P / \partial V - 2/3 P/V^2)] \quad (15)$$

Hilderbrand Equation of state [16] can be used to express  $\gamma$  and  $q$  in terms of derivatives of potential energy function.

For crystals with antiferrofluoride structure

$$P = -\partial\Phi/\partial V = (-1/3kr^2) \Phi'(r) \quad (16)$$

$$\partial P / \partial V = (-1/9k^2 r^4) (\Phi'' - 2/r \Phi') \quad (17)$$

$$\partial^2 P / \partial V^2 = (-1/27k^3 r^6) [\Phi''' - 6/r \Phi'' + 10/r^2 \Phi'] \quad (18)$$

$$\partial^3 P / \partial V^3 = (-1/81k^4 r^8) [\Phi'''' - 12/r \Phi''' + 52/r^2 \Phi'' - 80/r^3 \Phi'] \quad (19)$$

Where the primes denote the derivatives of  $\Phi(r)$  with respect to interionic separation.

### Equation of state of chalcogenides

The high pressure behaviour of these crystals is investigated by determining the compression values of these crystals by using Murnaghan logarithmic equation of state expressed as

$$V/V_0 = \exp[(-1/B'_0) \log_e \{(PB'_0/B_0) + 1\}] \quad (20)$$

Where  $B_0$  and  $B'_0$  are isothermal bulk modulus and its pressure derivatives, both referred to zero pressure [21]. The high pressure behaviour of these crystals have been shown below in figures 1.

## RESULTS AND DISCUSSION

The latest information on alkali chalcogenide crystals is far from complete but this work tries to add a little to the knowledge of these crystals by predicting

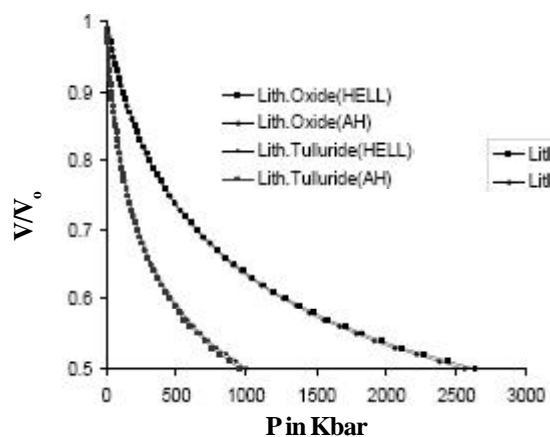


Figure 1 : A compression curves  $V/V_0$  pressure  $P$  (Kbar) for chalcogenide crystals based on our interionic potential models

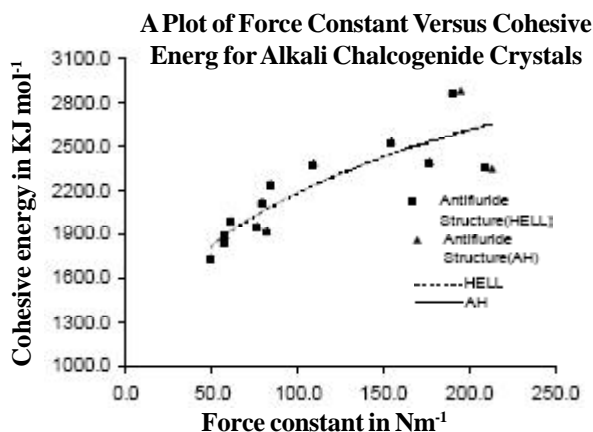


Figure 2

TABLE 1: Calculated properties of chalcogenide crystals cohesive energy (KJ mole<sup>-1</sup>) and calculated values

Crystal	HELL	AH	CAL.VAL <sup>[20]</sup>	CAL.VAL <sup>[17]</sup>
Li <sub>2</sub> O	2860.77	2879.18	2879.94	-
Na <sub>2</sub> O	2523.26	2537.53	2480.52	2535.12
K <sub>2</sub> O	2324.32	2332.88	2283.96	2244.9
Rb <sub>2</sub> O	2308.11	2313.64	2265.06	2160.48
Li <sub>2</sub> S	2372.08	2387.53	2393.16	2483.46
Na <sub>2</sub> S	2107.09	2121.03	2118.48	2209.2
K <sub>2</sub> S	1941.47	1952.72	1926.96	1992.06
Rb <sub>2</sub> S	1912.55	1922.66	1892.94	1942.92
Li <sub>2</sub> Se	2227.65	2243.04	2250.78	-
Na <sub>2</sub> Se	1983.52	1997.48	1998.78	-
K <sub>2</sub> Se	1828.15	1840.17	1821.96	-
Li <sub>2</sub> Te	2106.58	2120.45	2124.36	-
Na <sub>2</sub> Te	1882.84	1895.31	1898.40	-
K <sub>2</sub> Te	1727.64	1738.79	1734.60	-

TABLE 2 : Calculated properties of chalcogenide crystals (a) Force Constant  $f$  (Nm<sup>-1</sup>), (b) I.R. Absorption Frequency  $\nu_0$  (10<sup>12</sup> Hz) and (c) Debye Temperature  $\theta_D$  (K)

Crystal	F.C.	I.R.F.	D.TEMP
Li <sub>2</sub> O	17.35	23.21	1114.61
Na <sub>2</sub> O	15.45	15.75	756.35
K <sub>2</sub> O	17.66	15.36	737.38
Rb <sub>2</sub> O	23.34	16.21	778.09
Li <sub>2</sub> S	10.95	16.99	815.86
Na <sub>2</sub> S	7.95	9.48	455.18
K <sub>2</sub> S	7.66	8.11	389.58
Rb <sub>2</sub> S	8.19	7.29	350.22
Li <sub>2</sub> Se	8.43	14.09	676.68
Na <sub>2</sub> Se	6.16	7.24	347.50
K <sub>2</sub> Se	5.72	5.76	276.42
Li <sub>2</sub> Te	7.95	13.47	646.65
Na <sub>2</sub> Te	5.77	6.70	321.54
K <sub>2</sub> Te	4.94	5.00	240.04

several crystalline state properties such as cohesive energy (W), force constant, I.R. absorption frequency ( $\nu_0$ ), Debye temperature, Anderson-Grüneisen parameter ( $\delta$ ), Moelwyn-Hughes parameter ( $C_1$ ) and second

TABLE 3 : Calculated properties of chalcogenide crystals values of Gruneisen parameter ( $\gamma$ : dimensionless), Anderson Gruneisen parameter ( $\delta$ : dimensionless), Moelwyn-Hughes parameter  $C_1$  and second Gruneisen parameter ( $q$ : dimensionless)

Crystal	$\gamma_{HELL}$	$\gamma_{AH}$	$\delta_{HELL}$	$\delta_{AH}$	$C_1_{HELL}$	$C_1_{AH}$	$q_{HELL}$	$q_{AH}$
Li <sub>2</sub> O	1.20	1.17	2.40	2.34	3.40	3.34	0.22	0.22
Na <sub>2</sub> O	1.55	1.49	3.09	2.98	4.09	3.98	0.39	0.46
K <sub>2</sub> O	2.19	2.12	4.39	4.23	5.39	5.23	0.67	0.79
Rb <sub>2</sub> O	2.86	2.78	5.72	5.55	6.72	6.55	0.91	1.06
Li <sub>2</sub> S	1.32	1.28	2.65	2.55	3.65	3.55	0.30	0.33
Na <sub>2</sub> S	1.36	1.31	2.73	2.62	3.73	3.62	0.35	0.40
K <sub>2</sub> S	1.67	1.60	3.34	3.19	4.34	4.19	0.48	0.57
Rb <sub>2</sub> S	1.85	1.77	3.70	3.55	4.70	4.55	0.56	0.66
Li <sub>2</sub> Se	1.22	1.18	2.44	2.36	3.44	3.36	0.30	0.32
Na <sub>2</sub> Se	1.26	1.21	2.52	2.42	3.52	3.42	0.34	0.38
K <sub>2</sub> Se	1.50	1.43	3.00	2.87	4.00	3.87	0.42	0.49
Li <sub>2</sub> Te	1.37	1.31	2.73	2.63	3.73	3.63	0.34	0.38
Na <sub>2</sub> Te	1.39	1.33	2.77	2.66	3.77	3.66	0.36	0.41
K <sub>2</sub> Te	1.53	1.46	3.06	2.92	4.06	3.92	0.44	0.52

Grüneisen parameter ( $q$ ) respectively.

Hellmann and Ali-Hasan forms of short-range repulsive potential have been used to compute  $W$  of chalcogenide crystals and their values are listed in TABLE 1. It is found that the cohesive energy of a AO > AS > ATe > A Te for both the models. Only a few attempts have been made<sup>[17,18]</sup> to determine their cohesive energy using Born-Mayer model<sup>[19]</sup>.

The present values of  $W$  compare well with the calculated values of Jain-Shanker<sup>[20]</sup> and Morris<sup>[17]</sup>. It is observed that the inclusion of van der Waals terms improves the results expectedly and given the better agreement. Out of the two Hellmann and Ali-Hasan models, the latter presents a better result. Atomization energy are not reported for these crystals mainly because of the uncertainties in the values of electron affinities for chalcogenide ions.

TABLE 2 lists the calculated values of  $f$ ,  $\nu_0$  and  $\theta_D$ . And no comparison can be had for the agreement between the theoretical and experimental values as the experimental values are not available in the literature. The present calculation shows that van der Waals energy is important for heavier crystals. It is observed that the two models give almost identical results of  $f$ ,  $\nu_0$  and  $\theta_D$ .

The calculated values of  $\gamma$ ,  $\delta$ ,  $C_1$  and  $q$  have been listed in TABLE 3. There is no experimental data to draw comparison. But the present results indicate that  $\gamma$  depends upon the specific volume since the values tend to increase as we move from oxides to tellurides.

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We have investigated the high pressure behaviour of these crystals. The equation works well up to very high pressure. The compression curves are given in figure 1. The graphical behaviour of force constant and cohesive energy is shown in figure 2. The experimental data for the compressions of chalcogenide crystals are not available in the literature and hence it is not possible to draw experimental curves for these crystals. The theoretical results reported here may be useful for experimentalists in crystals of alkali chalcogenides.

### CONCLUSION

Hellmann and Ali-Hasan forms of interaction potential have been applied to get different crystalline state properties of chalcogenide crystals. The latter model gives encouraging result and may prove useful for further computation of the properties of such crystals.

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