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Theoretical Evaluation some Properties (Grűneisen parameter, Second Grűneisen parameter, Anderson Grűneisen parameter) of Alkali Chalcogenide Crystals (Selenides and Tellurides) using two interaction potential energy functions (IPEFs)

BISWAJIT GHATAK

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Abstract

In the analysis of crystal binding based on the interionic force model, the contributing arising from coulomb interactions, the dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions and the short-range repulsive interactions of the Hellmann and Varshni-Shukla interaction potential model.The different crystalline properties such as Grűneisen parameter Anderson Grűneisen parameter using two different formula for each parameter and Second Grűneisen parameter are reported here for alkali chalcogenide crystals(Selenides and Tellurides) of NaCl-structure. The high pressure behaviour of these crystals has also been studied. The graphical natures of calculated values I.R. absorption frequency-reduced mass and calculated values Debye temperature-reduced mass are also shown. The results obtained here may add a little to the physics and chemistry of these crystals.

Key words: Grűneisen parameter, Second Grűneisen parameter, Anderson Grűneisen parameter, high pressure behaviour of the crystals *etc.*

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 workers[1,2] have performed first principles *ab initio* calculations for potentials in ionic crystals. These calculations are based on the theory of Gordon and Kim[3] determining pair potentials for closed-shells system from the charge densities of the free ions constituting the crystal. The method of Gordon and Kim is essentially based on the Thomas-Fermi-Dirac electron gas model, which has been criticized, by Eggenhoffner, Murthi and Gumi[4], pointing out the lack of any self consistency of treatment between electron density and potential. Due to the simplifying approximations and the parameter-free nature of the first principles calculations, the results are generally less accurate than those derived from the parameterized models of the solids. These model potentials play a useful role in interpreting experimental results.

A number of short range potentials functions[5-16] have been proposed from time to time by different investigators. In the present study, Hellmann (Hell)[10], Varshni-Shukla (VS)[11] forms of short-range repulsive potential (SRRP) models are employed with an aim to establish that they could be the right forms of the forces responsible for the origin of the bounding in solids. For this the computation of various crystalline state properties like Grűneisen parameter, Second Grűneisen parameter, Anderson Grűneisen parameter, of the diatonic ionic crystals, *i.e.*, alkali chalcogenide crystals (selenides and tellurides) is needed and from their compatibility with the calculated values it would be possible to assert the right kind of the bounding forces. This investigation extends up to the evaluation of the equation of state as well as the an-harmonicity of the solids. The reason for selecting these models lies in their suitability[17] of evaluating their state properties as well as molecular state properties. Moreover, these potentials fulfill the fundamental physical requirements of an ideal potential.

The mathematical development of short range repulsive forces (SRRF) is the following form

Hellmann (Hell): $\phi_R(r) = \frac{S_1}{r}\exp\left(\frac{-r}{\rho_1}\right)$

Varshni-Shukla (VS): $\phi_R(r) = \frac{S_2}{r^2}\exp\left(\frac{-r}{\rho_2}\right)$

Method of Analysis:

The crystal lattice energy per ion pair can be expressed as

$$\phi_{total}(r) = \phi_c(r) + \phi_v(r) + \phi_R(r) \qquad (1)$$

Here $\Phi_c(r)$ is the long-range electrostatic coulomb energy with Madelung constant A. It is given by

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

Where z_1e and z_2e are the electrostatic charges on the ion pairs and r is the interionic separation.

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

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

Where C and D are vanderWaals (vdw) dipole-dipole and dipole quadrupole co-efficients are given by Tosi[1] Shankar, Singh and Agarwal[36]

The last term $\Phi_R(r)$ on the R.H.S. equation (1) is expressed as

$$\phi_R(r) = \frac{S_{ij}}{r^m}\exp\left(-\frac{r^n}{\rho}\right) \qquad (4)$$

Where S_i and ρ_i are potential parameters evaluated by applying the following crystal stability conditions:

$$\Phi'(r_o) = 0$$

and $$\Phi''(r_o) = 9kr_o/\beta \quad (5)$$

Where, k = crystals structure constant and β = isothermal compressibility.

In the above equations r_o is the equilibrium interionic separation in the lattice and the primes denote derivatives with respect to r.The general expression for repulsive strength parameter S_i and hardness parameter (ρ_i). The expressions for S_i and ρ_i are summarized as:

$$\Rightarrow S_{ij} = \frac{r_o^m\left[\frac{AZ_1Z_2e^2}{r_o} + \frac{6C}{r_o^8} + \frac{8D}{r_o^8}\right]}{\exp\left(\frac{-r_o^n}{\rho}\right)\left(m + \frac{nr_o^n}{\rho}\right)}$$

$$\Rightarrow \frac{1}{\rho_i} = \frac{X + n - 2m + 1 + \sqrt{(X + n - 2m - 1)^2 - 4m(m + 1 - X)}}{r_o^n 2n}$$

$$\Rightarrow X = \frac{9Kr_o^3 + \frac{2AZ_1Z_2e^2}{r_o} + \frac{42C}{r_o^6} + \frac{72D}{r_o^8}}{\left(\frac{AZ_1Z_2e^2}{r_o} + \frac{6C}{r_o^6} + \frac{8D}{r_o^8}\right)}$$

The last term Φ_R eq. (1) is the short-range overlap repulsive energy dominant in diatomic crystals. m = 1, n =1 for HM model; m = 2, n =1for VS model.

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 Columbian 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_o). This repulsive force in an ion becomes dominant at a very short distance, so it is known as short-range repulsive potential (SSRP). The exact form of SSRP in literature is still lacking.

Grüneisen Parameter:

The Grüneisen parameter γ is an important dimensionless parameter, which is a measure of anharmonicity in solids. The introduction of this parameter is required to describe the temperature dependence of the equation of state of solid.

Attempts[18- 23] been made to evaluate γ from the equation of state of solids but the agreement between the experimentally determined and calculated values is not satisfactory for different crystals other than other studies. An independent method to evaluate average value for a group of metals or alloys or compounds having the same crystal structure and bond type has been suggested by Bansigir[24].

The Grüneisen parameter γ describes the thermodynamic behavior of the crystals, was evaluated by Slater[25] from the theory of elasticity. His expression for the vibrational velocities is valid only if the solid is under zero external pressure. Dugdale and MacDonald[26] derived a more general expression for γ by including the effect of pressure. The Slater's theory as well as the formulation of Dugdale-Mac Donald is based on the approximation that Poisson's ratio is independent of volume. Simplified versions of the Grüneisen parameters for the present investigation obtained from Slater theory and DM theory are expressed as[27]

$$\gamma_{DM} = -\frac{r_o}{6}\left[\phi'''(r_o)/\phi''(r_o)\right] \tag{6}$$

$$\gamma_S = -\frac{2}{3} - \frac{r_o}{6}\left[\frac{\phi'''(r_o)}{\phi''(r_o)}\right] \tag{7}$$

Second Grüneisen Parameter:

The Grüneisen parameter and its first order volume dependence commonly referred to as the Second Grüneisen parameter are fundamental to the study of many basic phenomena in solids. The Grüneisen parameter is, in general, a function of both temperature and volume. It is well known [Vetelino *et al.*[28]] that the temperature dependence of Grüneisen parameter for a large number of diatomic crystals can be determined fairly accurately either experimentally or theoretically. The first order volume dependence of Grüneisen parameter is commonly known as the second Grüneisen parameter. It constitutes an additional measure of the anharmonicity in a solid. The Grüneisen parameter is itself being the first measure. Davies and Parkes[29] were the first to explicitly define the Second Grüneisen parameter as

$$q = \left(\frac{d\ln\gamma}{d\ln V}\right)_T \tag{8}$$

The uses of this parameter have been studied by various workers while dealing with the theory of temperature and pressure dependence of compressibility[30], the geophysical understanding of earth's interior[31,32], thermoelastic and dielectric behaviors of solids[33-36] and in theories of shock wave propagation[37].

In the present investigation an attempt has been made to compute the Grüneisen parameter as well as the Second Grüneisen parameter. Using expression based on higher order derivatives of an interaction potential within the frame work of Dugdale and MacDonald[26] theory

The second Grüneisen parameter (q) derived from this above equation (8) is written as

$$q_{DM} = \left(\frac{\partial\ln\gamma}{\partial\ln V}\right) = -\frac{V}{2\gamma}\left[\left(\frac{\partial^2 P}{\partial V^2} - \frac{10P}{9V^2}\right)\left(\frac{\partial P}{\partial V} + \frac{2P}{3V}\right) + V\left(\frac{\partial P}{\partial V} + \frac{2P}{3V}\right)^{-1}.\right.$$
$$\left.\left(\frac{\partial^3 P}{\partial V^3} - \frac{10}{9V^2}\frac{\partial P}{\partial V} + \frac{20}{9}\frac{P}{V^3}\right) - V\left(\frac{\partial^2 P}{\partial V} - \frac{10P}{9V^2}\right)\left(\frac{\partial P}{\partial V} + \frac{2P}{3V}\right)^{-2}\left(\frac{\partial^2 P}{\partial V^2} + \frac{2}{3V}\frac{\partial P}{\partial V} - \frac{2}{3}\frac{P}{V^2}\right)\right] \tag{9}$$

When the solid is under no external pressure, we have from eqn. (9)

$$q_{DM} = -\frac{V}{2\gamma}\left[\left(\frac{\partial^2 P}{\partial V^2}\right)\left(\frac{\partial P}{\partial V}\right)^{-1} + V\left(\frac{\partial P}{\partial V}\right)^{-1} . \left(\frac{\partial^3 P}{\partial V^3} - \frac{10}{9V^2}\frac{\partial P}{\partial V}\right) - V\left(\frac{\partial^2 P}{\partial V^2}\right)\left(\frac{\partial P}{\partial V}\right)^{-2} . \left(\frac{\partial^2 P}{\partial V^2} + \frac{2}{3V}\frac{\partial P}{\partial V}\right)\right] \tag{10}$$

Using Hildebrand equation of state[38], it is possible to express γ and q in terms of derivatives of potential energy function for crystals with NaCl structure.

$$P = -\frac{\partial \phi}{\partial V} = -\frac{1}{3Kr^2}\phi' ;$$

$$\frac{\partial P}{\partial V} = -\frac{1}{\left(3Kr^2\right)^2}\left[\phi'' - \frac{2}{r}\phi'\right];$$

$$\frac{\partial^2 P}{\partial V^2} = -\frac{1}{\left(3Kr^2\right)^3}\left[\phi''' - \frac{6}{r}\phi'' + \frac{10}{r^2}\phi'\right];$$

$$\frac{\partial^3 P}{\partial V^3} = -\frac{1}{\left(3Kr^2\right)^4}\left[\phi'''' - \frac{12}{r}\phi''' + \frac{52}{r^2}\phi'' - \frac{80}{r^3}\phi'\right]$$

Here the primes denote the derivatives of $\phi(r)$ with respect to, the interionic separation.

Anderson-Grüneisen Parameter:

Wachtman, Tefft, Lam and Apstein[39] measured Young's modulus for several inorganic oxide compounds as a function of temperature. They found that the modulus data can be adequately represented.

From theoretical considerations, Anderson[40] has derived a relationship, which relates the temperature dependence of the bulk modulus as a function of the specific heat and atomic volume. So Anderson Grűneisen parameter (δ) was introduced by Anderson[30]. The Anderson Grűneisen parameter can be express as

$$\delta = -\frac{r_o}{3}\left[\phi'''(r_o)/\phi''(r_o)\right] \tag{11}$$

According to Sharma[41] has derived similar for δ for a solid expression, which is written as

$$\delta = 2\gamma + \frac{1}{3} \tag{12}$$

Equation of State:

We have also investigated the high pressure behavior of these crystals by determining the compression values for these crystals with the help of Murnaghan logarithmic equation of state expressed as

$$\frac{V}{V_o} = \exp\left[-\frac{1}{B_o'}\log\left(P\frac{B_o'}{B_o} + 1\right)\right] \tag{13}$$

Where B_o and B_o' are the isothemal bulk modulus and its pressure derivative, both referred to zero pressure. This equation works well up to very high pressure[40]. The values of P corresponding to various compressions V/V_o are plotted using our calculated values of B_o and B_o'. According to theoretical compression curve (Srivastava *et al.* [42]) the high pressure behavior of the crystals have been shown in figure 1 and figure 2.

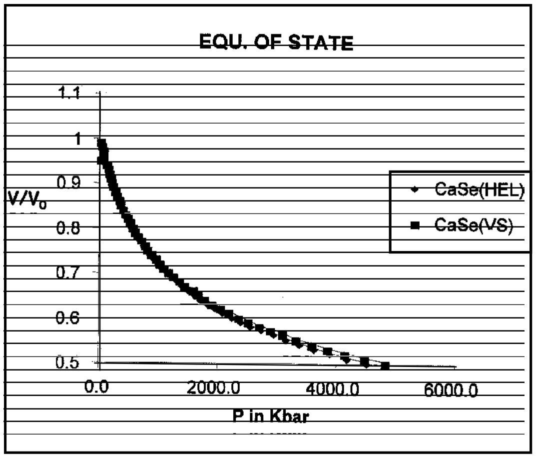

Figure 1

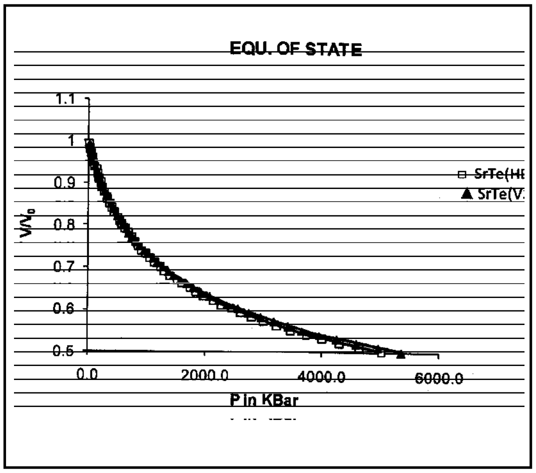

Figure 2

Discussion

Table 1 concerned with the evaluated values of alkaline earth chalcogenides crystals for different two potentials functions by employing equation (6),(7) for Grüneisen Parameter (GP) and equation (10) for Second Grüneisen Parameter(SGP). The experimental values are not found in literature. So it is difficult to conclude the degree of accuracy of our results and suitability of these models. The calculated values of Grüneisen Parameter (GP) and Second Grüneisen Parameter (SGP) match that those of these Parameter evaluated by Thakur[46].

The computated values of Anderson-Grüneisen Parameter (AGP) are given for these crystals with NaCl structure in Table no. 2 for different two potentials functions by employing equation (11) and equation (12). The experimental values are not available in literature. The calculated values AGP by Thakur[46] of is also reported.

It is found that the present values of GP in a narrow band about the value $\gamma < 3$ for these crystals for alkali metal halides the values of γ vary around the value $\gamma = 2$. The value of γ depends upon the specific volume and they increase, as rule, as we move towards the heavier crystals. Thus it can be said that the present values of γ are acceptable. It may be said that these potential function, which are well tested for alkali halides are acceptable for alkaline earth oxides and sulfides also.

The graphical behavior of reduced mass and I.R. Frequency (Figure 3), reduced mass versus Debye Temperature (Figure 4) are also shown.

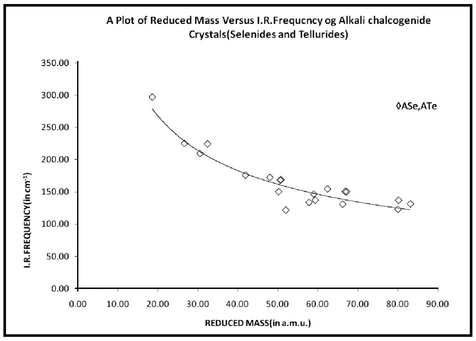

Figure 3

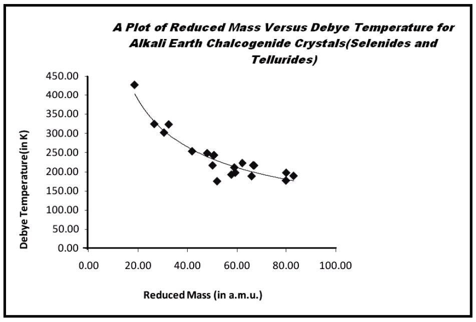

Figure 4

CALCULATED VALUES OF **GRÜNEISEN PARAMETER** *[dimensionless] EMPLOYING* ***DM [*** γ_{DM} *;eqn.(6)] AND* ***SLATER[***γ_s*;eqn.(7)] THEORY* **and SECOND GRÜNEISEN PARAMETER** [dimensionless] EMPLOYING ***EQUATION(10)*** OF TWO DIFFERENT MODELS *FOR* **ALKALI EARTH CHALCOGENIDE(Selenides and Tellurides) CRYSTALS**

	γ_{DM}	γ_{DM}	γ_s	γ_s	**Cal. VAL.**[a]	**q**	**q**
MgSe	1.08	1.17	1.42	1.50	1.85	1.08	0.85
CaSe	1.12	1.20	1.46	1.54	1.85	1.04	0.83
MnSe	0.95	1.06	1.28	1.39	1.85	1.69	1.24
SrSe	1.23	1.30	1.56	1.64	1.93	0.93	0.78
SnSe	1.15	1.24	1.48	1.57	1.86	1.18	0.94
BaSe	1.26	1.33	1.59	1.66	1.87	0.92	0.77
LaSe	1.17	1.26	1.51	1.59	1.87	1.17	0.94
CeSe	1.09	1.19	1.43	1.52	1.82	1.36	1.05
PbSe	0.58	0.74	0.91	1.07	2.02	4.87	2.94
ThSe	0.68	0.83	1.01	1.16	1.80	3.90	2.47
USe	0.28	0.48	0.61	0.82	1.76	1.45	1.51
CaTe	1.30	1.37	1.63	1.70	1.98	0.91	0.77
SrTe	0.89	0.99	1.22	1.33	1.84	1.61	1.17
SnTe	1.31	1.38	1.64	1.72	1.96	1.05	0.87
BaTe	1.41	1.47	1.75	1.81	2.02	0.87	0.75
LaTe	1.37	1.45	1.71	1.78	2.00	1.00	0.84
CeTe	1.33	1.41	1.66	1.74	1.74	1.06	0.88
PbTe	1.02	1.13	1.35	1.47	2.01	1.85	1.35
BiTe	1.34	1.42	1.67	1.75	2.02	1.11	0.92
UTe	0.98	1.11	1.32	1.45	1.94	2.11	1.50

(a) Thakur [46]

TABLE 2

CALCULATED VALUES OF **ANDERSON-GRÜNEISEN PARAMETER** *[dimensionless] OF TWO DIFFERENT MODELS EMPLOYING* ***equation(11)*** *AND* ***equation(12)*** *FOR* **ALKALI EARTH CHALCOGENIDE(Selenides and Tellurides) CRYSTALS**

Crystal	**HELL**	**VS**	**HELL**	**VS**	**Cal. VAL.**[a]
MgSe	2.17	2.33	2.50	2.67	3.70
CaSe	2.24	2.41	2.58	2.74	3.64
MnSe	1.90	2.11	2.23	2.45	3.70
SrSe	2.46	2.61	2.80	2.94	3.86
SnSe	2.30	2.47	2.63	2.80	3.72
BaSe	2.52	2.66	2.85	3.00	3.74
LaSe	2.35	2.52	2.68	2.85	3.74
CeSe	2.18	2.38	2.52	2.71	3.70
PbSe	1.16	1.48	1.50	1.81	4.04
ThSe	1.36	1.66	1.69	2.00	3.60
USe	0.56	0.97	0.90	1.30	3.52
CaTe	2.60	2.74	2.93	3.07	3.96
SrTe	1.77	1.99	2.10	2.32	3.68
SnTe	2.61	2.77	2.94	3.10	3.92
BaTe	2.82	2.95	3.16	3.28	4.04
LaTe	2.75	2.9	3.08	3.23	3.99
CeTe	2.66	2.82	2.99	3.15	3.48
PbTe	2.03	2.27	2.36	2.60	4.02
BiTe	2.67	2.84	3	3.17	4.04
UTe	1.97	2.22	2.3	2.56	3.82

(a)Thakur [46]

The Grüneisen parameter is usually defned by the relation,

$$\gamma = -\frac{d(\log \Theta_D)}{d(\log V)}$$

this readily leads to the equation

$$\log \Theta_D = -\gamma \log V + C \qquad (12)$$

Where Θ_D is the Debye temperature and C the constant of integration. Equation (12) is valid for a given substance for which γ is a constant. So it is clear that the graph of $\log \Theta_D$ Versus $\log V$ is linear^{47}.

Conclusion

It is difficult to conclude degree of accuracy of our results and suitability of models. A simple cursory look into these tables establishes that our models give comparatively better results and explain the anharmonic behavior of solids[45]. It may be said that these potential functions [Hellmann (Hell), Varshni-Shukla (VS)] forms which are well tested for alkali metal halides[43], alkali metal hydrides[44] are acceptable for alkali earth selenides and tellurides also. The latter model gives encouraging result and may prove useful for further computation of the properties of such crystals.

The computation of Grüneisen Parameter and Second Grüneisen Parameter proves to be important additional parameter for the evaluation of anharmonicity in solids. The evaluation of equation of a state of diatomic ionic crystal enables to discover that the systems under investigation are compressible upto very high pressure. The theoretical results of some crystals (no experimental values available in literature) may useful for experimentalists.

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