

High Pressure Structural Properties of Rare-earth Antimonide

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Abstract

In the present paper, we have investigated the high-pressure structural phase transition of rare-earth antimonide. We studied theoretically the structural properties of this compound (DySb) by using the three-body potential model with the effect of electronic polarizability (TBIPE_p). These compounds exhibits first order crystallographic phase transition from NaCl (B₁) to CsCl (B₂) phase at 22.6 GPa respectively. The phase transition pressures and associated volume collapse obtained from present potential model(TBIPE_p) show a good agreement with available experimental data.

Keywords: High Pressure, Crystal Structure, Volume Collapse

1. Introduction

The mono-antimonide of rare earths with NaCl structure in recent years have drawn great attention of condensed matter scientists because of their diverse and unusual properties, in respect of structural, magnetic and vibrational properties [1]. So far as the structural properties are concerned, several pnictides of lanthanide group, which crystallize in NaCl (B₁) type crystal structure have been investigated by using high-pressure X-ray diffraction technique [2-5] and reported to undergo to either CsCl (B₂) or body centered tetragonal structure. These partially filled f-electron shells of the lanthanide ions are highly delocalized and therefore interact strongly with the lattice. Such behaviour has been interpreted in terms of promotion of 4f electron of rare earth ion to the 5d conduction band and the mixing of f states with the p states of the neighbouring ion. The electronic band structures of NdY and CeY (Y:pnictogen) have been calculated by De et al.[6] using self consistent semi relativistic Linear Muffin-Tin Orbital Method reveals that the unusual properties are due to strong mixing of f-states of rare earth ion with the p-orbital of pnictogen ion (p-f mixing) [6,7]. The high pressure form of lighter lanthanide antimonides (RESb, RE=La,Ce, Pr and Nd) is reported to be body centered tetragonal where as the structure of middle RESb (RE=Sm, Gd and Tb) is unknown. The heavier RESb (RE= Dy, Ho, Er, Tm and Lu) show B₁- B₂ phase transition [8].

In the present paper we have investigated the high-pressure structural phase transition, cohesive and elastic properties of rare earth antimonide DySb. We have employed our three body interaction potential with the effect of electronic polarizability(TBIPE_p) approach to study high pressure behavior. The present three body potential model includes the long range Columbic, three body interaction, short range overlap repulsive interaction operative up to second neighbor ions within Hafemeister and Flygare approach [9] and electronic Polarizabilities effect. The importance of inclusion short range (SR), and electronic polarizability has been established in our work.

2. Potential Model and Method of Calculation:

It is well known that the application of pressure on crystals results a change in its volume that leads to an increased charge transfer (or three-body interaction effects) due to the deformation of the overlapping electron shells of the adjacent ions. The three body interaction arises during lattice vibrations when electron shells of neighboring ions overlap. This overlapping leads to the transfer of charge which interacts with other charges and many body interaction (MBI) takes place, the dominant part of which is the three body interaction. This interaction becomes more important due to the decrease in inter ionic spacing of the lattice crystal when pressure gets increased and when anions experience sufficient overlap. Besides, both an enhancement in overlap energy and the transferred charge due to the overlap in electron shells modify the ionic charge, which in its turns modifies the Coulomb energy. The expression for the modified Coulomb energy due to three body interaction (TBI) is

$$\Phi_m(r_0) = \Phi^c + \Phi^T \quad (1)$$

$$\Phi_m(r_0) = [-\alpha_M Z^2 e^2 / r] [1 + (2n/Z) f(r_0)] \quad (2)$$

Here α_M is the Madelung constant (for NaCl and for CsCl structure solids), r_0 is the equilibrium nearest neighbor (nn) ion separation, n is the number of nearest neighbor (nn), and $f(r)$ is the TBI parameter which is dependent on the nearest neighbor distance (r) as

$$f(r) = f_0 \exp(-r/\rho) \quad (3)$$

These effects have been incorporated in the Gibbs free energy ($G=U+PV-TS$) as a function of pressure (P). Here, U is the internal energy, which at T= 0 K is equivalent to the lattice energy and S is the vibrational entropy at absolute temperature T. Since theoretical calculations are done at T= 0 K, the Gibbs's free energy is equivalent

to enthalpy. At $T = 0$ K and pressure P , the Gibbs free energies for NaCl(B1) and CsCl(B2) structures are given by

$$G_{B1}(r) = U_{B1}(r) + PV_{B1} \quad (4)$$

$$G_{B2}(r') = U_{B2}(r') + PV_{B2} \quad (5)$$

with V_{B1} and V_{B2} as the unit cell volumes for B1 and B2 phases, respectively. The first terms in the energies (4) and (5) are lattice energies for B1 and B2 structures and they are expressed as:

$$U_{B1}(r) = [-(\alpha_m z^2 e^2)/r] - [(12\alpha_m z e^2 f(r))/r] + (e^2 \alpha_c)/r^4 + 6b\beta_{ij} \exp[(r_i + r_j - r)/\rho] + 6b\beta_{ii} \exp[(2r_i - 1.41r)/\rho] + 6b\beta_{jj} \exp[2r_j - 1.41r)/\rho] \quad (6)$$

$$U_{B2}(r') = [-(\alpha'_m z^2 e^2/r')] - [(16\alpha'_m z e^2 f(r'))/r'] + (e^2 \alpha_c)/r'^4 + 8b\beta_{ij} \exp [(r_i + r_j - r')/\rho] + 3b\beta_{ii} \exp [(2r_i - r')/\rho] + 3b\beta_{jj} \exp [2r_j - r')/\rho] \quad (7)$$

Here, z is the ionic charge, r_i (r_j) is the ionic radii of i (j) ions, ρ is the range parameter, b is the hardness parameter, $f(r)$ is the three body interaction parameter, $r(r')$ is the inter ionic separation for B1 (B2) phases and ij is the Pauling coefficients defined as

$$\beta_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \quad (8)$$

where, z_i (z_j) and n_i (n_j) denote the valence and number of electrons in the outermost orbit of cations (anions). These lattice energies consist of long-range Coulomb energy (first term), three body interactions (second term), the electronic polarizability (third term) and the short range overlap repulsive interaction (fourth term). To calculate these parameters, we have employed the following equilibrium conditions.

$$[dU / dr]_{r=r_0} = 0 \text{ and } [d^2 U / dr^2] = 9k r_0 B_T \quad (9)$$

To understand elastic properties of this mono-pnictide, we have calculated second order elastic constants (SOEC) C_{11} , C_{12} and C_{44} , these elastic constants are functions of first and second order derivatives of short range potential, so their calculation will provide knowledge about the effect of short range forces on these materials following Shanker et al. [10]. The expression for SOE constants is given as:

$$C_{11} = e^2/4r_0^4 [- 5.112z \{z + 12f(r)\} + A1 + (A2 + B2)/ 2] + 9.30z (rdf/dr) \quad (10)$$

$$C_{12} = e^2/4r_0^4 [1.391z \{z + 12f(r)\} + (A2 - B2)/4 + 9.30z (rdf/dr)] \quad (11)$$

$$C_{44} = e^2/4r_0^4 [2.556z \{z + 12f(r)\} + B1 + (A2 + 3B2)/ 4] \quad (12)$$

We have followed the technique of minimization of $U_{B1}(r)$ and $U_{B2}(r')$ at different pressures in order to obtain their inter ionic separations r and r' corresponding to B_1 and B_2 phases. First, we have evaluated the corresponding Gibbs free energies $G_{B1}(r)$ and $G_{B2}(r')$ and their respective differences $\Delta G = (G_{B2}(r') - G_{B1}(r))$. Then, we have plotted ΔG against pressure (P), as shown in Fig. 1, for DySb. The phase transition pressure (P_t) is the pressure at which ΔG approaches zero.

3. RESULT AND DISCUSSION:

Using the measured values of the equilibrium lattice constant (r_0) and bulk modulus (B_T) with $K=2$ for B1 phase, the model parameters thus calculated are given in Table 1 and are used to compute the results presented and discussed below. For simplicity, we have taken account of only a single set [ρ , b , $f(r)$] in B1-phase and the same set is used in B2 phase. The reason for this is that during the phase transition from B1→B2 the atomic distribution takes a different arrangement and they get arranged in B2 structure after phase transition. Inter-ionic separation changes are calculated by the minimization technique. The parameter $f(r)$ is inter-ionic separation (r) dependent and it is therefore changed accordingly. We have followed the technique of minimization of $U_{B1}(r)$ and $U_{B2}(r')$ at different pressures in order to obtain their inter ionic separations r and r' corresponding to B_1 and B_2 phases. First, we have evaluated the corresponding Gibbs free energies $G_{B1}(r)$ and $G_{B2}(r')$ and their respective differences $\Delta G = (G_{B2}(r') - G_{B1}(r))$. Then, we have plotted ΔG against pressure (P), as shown in Fig. 1. The phase transition pressure (P_t) is the pressure at which ΔG approaches zero. We have also computed the relative volume changes $V(P)/V(0)$ and plotted them against the pressure as depicted in Fig.2. It is clear from Fig.1 that phase transition B1→ B2 occur at about 22.6GPa for DySb respectively, and the calculated volume collapses using TBIPe_p model are 3.8% for DySb. These are close to experimental and other theoretical values.

Finally, we have noticed that during the crystallographic transition from B1 to B2, the volume discontinuity in pressure-volume phase diagram identifies the same trends as the experimental data and these results are well fitted we have also stated the high pressure stability criterion for ionic crystal, the stable phase of a crystal is one in which the shear elastic constant C_{44} is non-zero (for mechanical stability) and which has the lowest potential energy among the mechanically stable lattices. Thus the stability of NaCl-type structure in terms of elastic constants should satisfy the following conditions

$$B_T = 1/3 (C_{11} + 2C_{12}) > 0, C_{44} > 0 \text{ and } C_S = (C_{11} - C_{12})/2 > 0 \quad (13)$$

The estimated shear moduli and tetragonal moduli are $C_{44} = 39.2$ GPa and $C_S = 53.9$ GPa for DySb which are well suited for the above elastic stability criterion for Rare-Earth antimonide (RESb) compound. From Table 3, our estimated C_{44} for DySb are positive and hence the above stability criterion is satisfied for ionic crystal.

Musgrave and Pople [11] pointed out that if either C_{44} or $C_S = (C_{11} - C_{12})/2$ goes to zero as the pressure is increased, then the structure becomes unstable and the crystal transforms by a spontaneous shear. Also, in the case of B1- structure, C_{44} decreases up to Pt but the phase transition to the B2 – structure takes place before the C_{44} reaches zero. Demarest et al. [12] proposed a slight modification of the Born stability criterion that a phase transition takes place when the ratio C_{44} / B_T reaches a critical value. We have computed elastic constants and plotted C_{44}/B_T with different pressures and hence the trends shown from TBIPe_p are consistent with the requisites of first-order phase transition. On the basis of above work, it is concluded that the TBIPe_p approach is adequately suitable for the prediction of B1→B2 phase transition pressures and associated volume collapses in RESb compound.

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Table 1. Input parameters and model parameters.

Compounds	Input Parameters			Model Parameters		
	r_0 (Å)	B_T (GPa)	α_c	$b(10^{-12}\text{ergs})$	ρ (Å)	$f(r)$
DySb	3.08	64.15	11.16	2.607	0.7043	0.0138

Table 2: Calculated elastic constants

Compounds	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
DySb	136present 141 others ^b	28.4 present 25.8 others ^b	39.2 present 26.2 others ^b

a. Ref [13]

b. Ref [14]

Table 3: Calculated transition pressures and volume collapses.

Compounds	Transition	Phase Transition Pressure (GPa)	Relative Volume change %
DySb	B1— B2	22.6 present >22 expt ^a	3.8 present 3.0 expt ^a

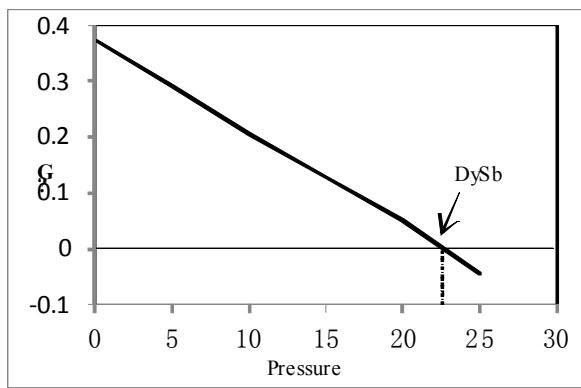


Fig.1. Variation of ΔG with Pressure

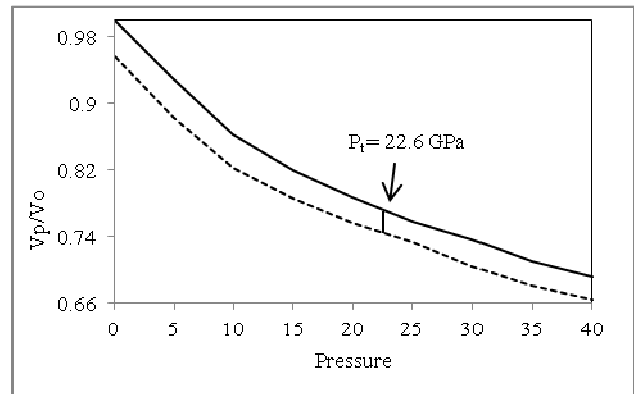


Fig.2. Variation of V_p/V_o with Pressure

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