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Theoretical prediction of high pressure structural phase transition in LaBi with NaCl structure

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ABSTRACT: In the present paper, we have investigated the high-pressure structural phase transition of lanthanum bismuthide. We studied theoretically the structural properties of this compound (LaBi) by using the three-body potential model with polarization (TBIPM). This compound exhibits first order crystallographic phase transition from NaCl (B1) to BCT phase at 22GPa. The phase transition pressures and associated volume collapse obtained from present potential model show a good agreement with available experimental data.

Keywords: Phase transition, Volume collapse, Three body potential and High pressure.

I. INTRODUCTION

Monopnictides of rare-earth elements (LnY, where Ln are lanthanides; Y = N, P, As, Sb, Bi) [1] have attracted attention of researchers due to the improvement of the technology of their preparation. As a proper reference material having no occupied 4f states, the lanthanum pnictides, LaBi has been investigated both experimentally and theoretically. The rare-earth pnictides, generally, have low carrier, strongly correlated systems [2], and they show dense Kondo behaviour and heavy fermion states [3–5].

Hasegawa [6] reported the electronic band structure of LaSb and LaBi. As far as LaBi is concerned, the bulk modulus data in the B1 phase is reported by Benedict [7]. The study on structural, electronic band structures, elastic and lattice dynamical properties of rare earth monopnictides CeBi and LaBi, using first-principles density functional calculations within the pseudopotential approximation by Mankad et al [8]. By use of synchrotron radiation, powder x-ray diffraction of LaBi with a NaCl-type structure has been studied up to 17 GPa at room temperature by Hayashi *et al* [9].

We have studied phase transition phenomena to study the phase transition in NaCl type lanthanum bismuthide compound using three-body potential model, which includes long range Columbic, three-body interaction and short-range overlap repulsive interactions. It is felt that this potential model is suitable for this group of compounds. The formulation of the present potential model and the method of calculations are described in the next section.

II. POTENTIAL MODEL

Application of pressure directly results in compression leading to the increased charge transfer due to the deformation of overlapping electron shell of the adjacent ions (or non rigidity of ions) in solids. These effects have been incorporated in the Gibbs free energy (G = U+PV-TS) as a function of pressure and three body interaction which are the most dominant among the many body interactions. Here, U is the internal energy of the system. At temperature T = 0K and pressure P the Gibbs free energies for NaCl (B1) and BCT structures are given by:

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}(r) \qquad \ldots(1)$$

$$G_{BCT}(r) = U_{BCT}(r) + PV_{BCT}(r) \qquad \ldots(2)$$

With V_{B1} and V_{BCT} as the unit cell volumes for B1 and BCT structures respectively. The first term in equation (1) and (2) are lattice energies for B1 and BCT structures and they are expressed as:

$$U_{B1}(r) = [-(\alpha_m z^2 e^2)/r] - [(12\alpha_m z\, e^2\, f(r))/r] + 6b\beta ij \exp[(ri + rj - r)/\rho] + 6b\beta ii \exp [(2ri - 1.41r)/\rho + 6b\beta jj \exp [2rj - 1.41r)/\rho] \qquad \ldots(3)$$

$$U_{BCT}(r') = [-(\alpha'_m z^2 e^2/r')] - [(16\alpha'_m z e^2 f(r'))/r'] + 8b\beta ij \exp[(ri + rj - r')/\rho] + 2b\beta ii \exp [(2ri - r')/\rho] + b\beta i \exp[(2ri - r'')/\rho] + 2b\,\beta jj \exp [(2rj - r')/\rho] + b\beta jj \exp[(2rj - r'')/\rho] \qquad \ldots(4)$$

Here, ze is the ionic charge, ri (rj) 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 is nearest neighbor (nn) separation for NaCl phase and r′ is the nearest neighbour distance corresponding to lattice parameters a and c in tetragonal structure and βij is the Pauling coefficients defined as

$$\beta_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \qquad \ldots(5)$$

where, zi (zj) and ni (nj) 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) and the short range overlap repulsive interaction (fourth term). To calculate these parameters, we have employed the following equilibrium conditions.

$[dU/dr]_{r=r0} = 0$ and $[d^2U/dr^2] = 9kr_0B_T$

To understand elastic properties of these mono-pnictides, we have calculated second order elastic constants (SOEC) C_{11}, C_{12} and C_{44} and their pressure derivatives at 0 K, since 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 material. The expression [10, 11] for SOEC is given as

$$C_{11} = e^2/4r_0^4 [- 5.112z \{z+12f(r)\} + A1 + (A2 + B2)/ 2]+ 9.30z (rdf/dr)] \quad \ldots(6)$$

$$C_{12} = e^2/4r_0^4 [1.391z \{z + 12f(r)\} + (A2 – B2)/4 + 9.30z (rdf/dr)] \quad \ldots(7)$$

$$C_{44} = e^2/4r_0^4 [2.556z \{z+12f(r)\} + B1 + (A2 + 3B2)/4)] \quad \ldots (8)$$

III. RESULTS

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 BCT phase. The reason for this is that during the phase transition from B1 → BCT the atomic distribution takes a different arrangement and they get arranged in BCT structure after phase transition. This arrangement affects interionic separation also. 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 $U_{BCT}(r')$ at different pressures in order to obtain their inter ionic separations r and r′ corresponding to B1 and BCT phases. First, we have evaluated the corresponding Gibbs free energies $G_{B1}(r)$ and $G_{BCT}(r')$ and their respective differences $\Delta G = (G_{BCT}(r') - G_{B1}(r))$. Then, we have plotted ΔG against pressure (P), as shown in Fig. 1, for LaBi.

Table 1: Input parameters and model parameters.

Compound	LaBi		
Input Parameter	r_0 3.282		B_T 55
Model parameter	b(10^{-12} ergs) 3.9645	ρ(Å) 0.7456	f(r) 0.0423

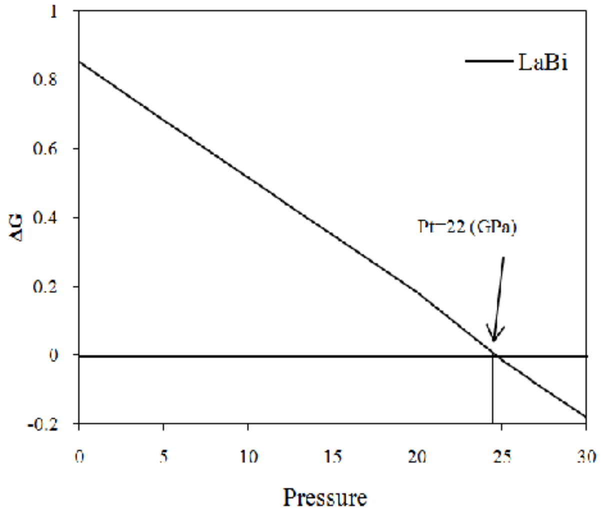

Fig. 1. Variation of ΔG with Pressure.

The phase transition pressure (Pt) is the pressure at which ΔG approaches zero. At this pressure both the phases coexist. ΔG is important factor in deciding the relative stability of phases. After phase transition system becomes stable in BCT phase. We have also computed the associated relative volume changes Vp/Vo which are given in Table 2 and plotted them against the pressure as depicted in Fig. 2 for LaBi.

Table 2: Calculated transition pressures and volume collapses.

Compounds	Phase Transition (GPa)	Relative Volume change (%)
LaBi	Pre – 22 Exp -17[9] Other -11.2 [12]	Pre- 2.3 - Other -8.9 [12]

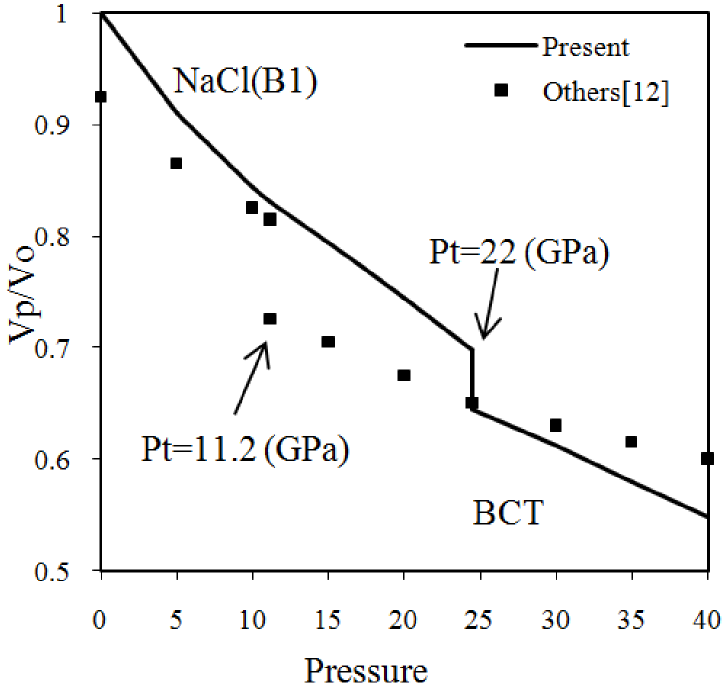

Fig. 2. Variation of Volume Change (Vp/Vo) with Pressure.

It is clear from Fig. 2 that phase transition B1→ BCT occurs at about 22 GPa LaBi, and the calculated volume collapse using TBIP model are 2.3 % for LaBi.

We have computed the second-order elastic constants (SOEC), which are shown in Table 3. 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. On the basis of above work, it is concluded that the TBIPM approach is adequately suitable for the prediction of B1→BCT phase transition pressure and associated volume collapse in LaBi compound.

Table 3: Calculated elastic constants.

Compounds		C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
LaBi	Present Others[13]	117.5 140.12	23.6 58.15	18.8 17.94

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