High Pressure Structural Properties of Cerium Monopnictide

Purvee Bhardwaj and Sadhna Singh

***Abstract*— In the present paper, we have investigated the high-pressure structural phase transition of cerium monopnictide. The three-body potential model has been used to study the structural properties of this compound. Phase transition pressures are associated with a sudden collapse in volume. The phase transition pressures and associated volume collapses obtained from present potential model show a generally good agreement with available experimental data than others.**

***Index Terms*— Pnictides, volume collapse, crystal structure, phase transition.**

I. INTRODUCTION

High-pressure research on structural phase transformations and behavior of materials under compression based on their calculations or measurements have become quite interesting in the recent few years. An example can be found in the rare earth (RE) chalcogenides and pnictides, where the structural optical and electrical properties at high pressure have been extensively studied [1-4]. The rare-earth pnictides have drawn considerable interest, both theoretically and experimentally because of their interesting semi conducting properties and various practical applications in the field of non-linear optics, electro-optic components, glass-making, grinding alloys, composites lasers, phosphors lasers, and electronics [1-6]. The rare-earth pnictides are considered to be part of the green technology industry, helping to improve energy efficiency in magnets, batteries, glass and computers. Due to the relatively gradual decrease in ionic size with increasing atomic number, the rare earth elements have always been difficult to separate. The rare earth (RE) chalcogenides and pnictides (REX; X =O, S, Se, Te and REY; Y =N, P, As, Sb and Bi) under go a phase transition from six fold coordinated NaCl to more closed eight fold coordinated CsCl structure [1-6].

In Cerium chalcogenides and pnictide compounds, only CeP has been found to undergo a first order phase transition (isomorphous) at about 10 GPa [2,3]. The theoretical work by Svane et al. [4] has further widened the scope of future theoretical and accurate experimental investigations of electronic and crystallographic transitions for these groups of compounds. In CeAs no iso-structural transition due to pressure induced valence change from 3p to 4p state of Ce-ion has been observed [5], and CeSb shows B1 to tetragonal phase transition, while CeBi transforms into CsCl structure at high pressure [6]. Further the smaller value of bulk modulus in CeBi and in CeTe as compared to other Cerium chalcogenides and pnictide compounds has also been ascribed to volume dependent Kondo effect [6]. Only a few theoretical papers and a little experimental work have been devoted to the study of structural and electronic properties of this series of rare earth pnictides.

Looking at the fact that these compounds are less explored, we applied our extended interaction potential (EIP) model to these compounds to study high pressure phase transition and other properties. The need of inclusion of three body interaction forces was emphasized by many workers for the betterment of results [7-9]. Earlier calculations for B1-B2 transitions were based on two-body potential mainly. They concluded that possible reasons for disagreements include the failure of the two body potential model. Since these studies were based on two body potentials and could not explain Cauchy violations ($C_{12} \neq C_{44}$). They remarked that results could be improved by including the effect of non-rigidity of ions in the model.

It is seen from the current literature that three body potential model (TBP) used and developed by Singh and coworkers [10-13] has been found to be remarkably successful in giving the unified description of structural and elastic properties of ionic and semi conducting crystals. In this TBP model, the three body interactions owe their origin to the quantum mechanical foundation and also to the phenomenological approach [10,14] in terms of the transfer (or exchange) of charge between the overlapping electron shells of the adjacent ions in solids. This TBP approach has been extended to include the Hafemeister-Flygare (HF) type [15] overlap repulsion operative upto the second neighbour ions for describing, the lattice static and mechanical properties of binary ionic solids and alloys. Also, Tosi and coworkers [16] have demonstrated the significance of vander Waals (*v*dW) attraction due to the dipole-dipole (d-d) and dipole-quadruple (d-q) interactions to describe the cohesion in ionic solids and they are generally ignored in the first principle calculations.

Motivated from the above mentioned success of the TBP model in III-V and II-VI compound semiconductor, we thought it pertinent to apply three body potential (TBP) model for the prediction of phase transition pressures and associated volume collapses in rare earth pnictides.

We have studied phase transition phenomena to study the phase transition in NaCl type cerium bismuth compound using three-body potential model, which includes long range Coulombic, three-body interaction and short-range overlap repulsive interactions. It is felt that this potential model is suitable for this group of compounds. The

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formulation of the present potential model and the method of calculations are described in section II. The results are presented and discussed in section III.

II. POTENTIAL MODEL AND METHOD OF CALCULATION

Application of pressure directly results in compression leading to the increased charge transfer of the overlapping of electron shells of the adjacent ions (or non-rigidity of ions) in solids [10]. These effects have been incorporated in the Gibbs free energy (G = U+PV-TS) as a function of pressure and three body interactions (TBI), which are the most dominant among the many body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At T=0 K temperatures the Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures are given by:

$$G_{B_1} = U_{B_1}(r) + PV_{B_1} = (2.0r^3) \qquad (1)$$

$$G_{B_2} = U_{B_2}(r') + PV_{B2} = (1.154r^3) \qquad (2)$$

Where first term, in above Esq. (1) and (2) represent lattices energies U_{B1} for B1 and U_{B2} for B2 structure, respectively. The expressions of lattices energies U_{B1} and U_{B2} are given:

$$\begin{aligned} U_{B_1} = {} & \frac{-\alpha_M Z^2 e^2}{r} - \frac{12\alpha_M Ze^2 f(r)}{r} \\ & + 6b\beta_{ij} \exp(r_i + r_j - r/\rho) \\ & + 6b\beta_{ii} \exp(2r_i + 1.41\, r/\rho) \\ & + 6b\beta_{jj} \exp(2r_j - 1.41\, r/\rho \qquad (3) \end{aligned}$$

$$\begin{aligned} U_{B_2} = {} & \frac{-\alpha'_M Z^2 e^2}{r'} - \frac{16\alpha'_M Z\ e^2 f(r')}{r'} \\ & + 8b\beta_{ij} \exp(r_i + r_j - r/\rho) \\ & + 3b\beta_{ii} \exp(2r_i + 1.154\, r/\rho) \\ & + 3b\beta_{jj} \exp(2r_j - 1.154\, r/\rho) \qquad (4) \end{aligned}$$

Here, first and second terms represent long-range Coulomb and TBI interactions. Third term corresponds to overlap repulsion given by Hafemeister Flygare [HF] with α_M and α_M' are the Madelung constant for B1 and B2 structures, respectively, β_{ij} is the Pauling coefficients, Ze is ionic charge with e as the electronic charge; b and ρ are the range and hardness parameters, f(r) and f′(r′) are TBI parameters for B1 (B2) phase. The TBI expressed as f (r) = $f_o$exp (-r/ ρ) with f_o as a constant.

Elastic properties of solids are closely related to many fundamental solid-state properties, such as equation of state (EOS), specific heat thermal expansion, Debye temperature, Gru¨neisen parameter, melting point and so on. From the elastic constants, one can obtain valuable information about the binding characteristic between adjacent atomic planes, and about the anisotropic character of the bonding and structural stability.

The knowledge of SOEC's and their pressure derivatives are important for the understanding of the interatomic force in solids. The expressions of second order elastic constants are as follows:

$$\begin{aligned} C_{11} = {} & (e^2/4a^4)[-5.112\, Z(Z + 12\, f(r)) + A_1 \\ & + (A_2 + B_2)/2 + 9.3204\, zaf\,'(r)] \end{aligned}$$

$$\begin{aligned} C_{12} = {} & (e^2/4a^4)[0.226\, Z(Z + 12\, f\ (r)) - B_1 \\ & + (A_2 - 5B_2)/4 + 9.3204\, zaf\,'\ (r)] \end{aligned}$$

$$\begin{aligned} C_{44} = {} & (e^2/4a^4)[2.556\ Z(Z + 12\ f\ (r)) \\ & - B_1 + (A_2 + 3B_2)/4 \end{aligned}$$

Using model parameter (b, ρ, *f(r)*), pressure derivatives of bulk modulus have been computed whose expressions are as follows:

$$\frac{dB}{dp} = -(3\Omega)^{-1} \begin{bmatrix} 13.980Z(Z + 12f(r)) + C_1 - 3A_1 + C_2 - 3A_2 \\ -167.7648zaf(r) + 41.9420za^2 f(r)] \end{bmatrix}$$

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad S = \frac{1}{2}(C_{11} - C_{12})$$

and

$$\Omega = -2.330Z(Z + 12f(r)) + A_1 + A_2 + 21.9612zaf\ (r)$$

The values of A_i, B_i, and C_i (i =1, 2) have been evaluated from the knowledge of b, ρ and vdW coefficients.

III. RESULTS AND DISCUSSION

The three-body potential model described in previous section contains three model parameters [b, ρ, f(r)], namely the hardness, range and three body force parameter. The values of these parameters have been evaluated using the first and second order space derivatives of the cohesive energy (U) expressed as:

$$[dU/dr]_{r=r_0}$$

$$[d^2U / dr^2] = 9kr_0 B$$

and the procedure prescribed in our earlier work [17-19].

The present potential model contain three model parameters [b, ρ, f (r)], namely hardness, range and three body force parameter. The input crystal data and calculated model parameters for the present compound are given in Table 1.

Table-1 Input parameters and generated model parameters for cerium pnictide.

Solid	Input Parameters		Model Parameters		
	r_0 (Å)	B_T (GPa)	b(10^{-12} ergs)	ρ	f (r)
CeBi	3.275	50.0	160.91	0.321	0.113

As, the stable phase is associated with minimum free energy of the crystal, we have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. We have minimized G_{B1} (r) and G_{B2} (r') given by Eqns. (3) and (4) at different pressures in order to obtain the interionic separations r and r' corresponding to B_1 and B_2 phases associated with minimum energies. The phase transition occurs when ΔG approaches zero (ΔG→0).

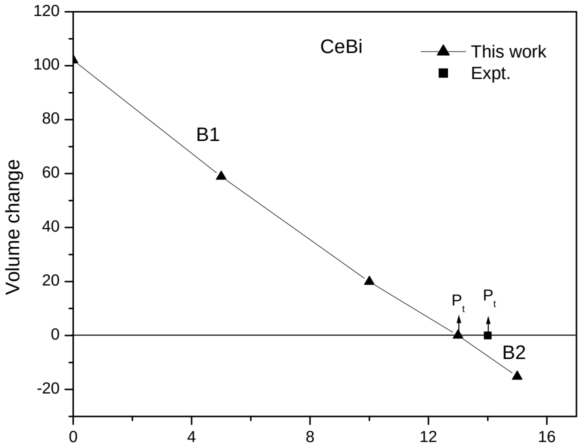

Fig: 1 Variation of ΔG (KJ/mol) with pressure for CeBi.

The phase transition pressure (P_t) is the pressure at which ΔG approaches zero. Fig.1 shows our present computed phase transition from NaCl-type [B_1] to CsCl-type [B_2] structure. The experimental value of phase transition pressure is 14.0 GPa and our calculated value of phase transition for CeBi is 13.0 GPa. The solid square (■) represents the experimental value of phase transition.

Table-2 Phase transition and volume change of cerium pnictide.

Solid	Phase Transition Pressure (GPa)		Volume Collapse %	
	Present	Expt.	Present	Expt.
CeBi	13.0	14.0^a	6.3	5.6^a

a-ref [3].

Relative volume changes V $_{(p)}$/V $_{(0)}$ have been plotted against pressure and depicted in Fig.2 for CeBi. At P_t these compounds undergo a (B1-B2) transition associated with a sudden collapse in volume showing a first order phase transition. The values of volume collapse (%) are given in Table-2. It is clear from Table 2 and Fig 2 that our calculated volume collapses -Δ V $_{(p)}$/V$_{(0)}$ for CeBi is 6.3 while the experimental value of volume collapse for CeBi is 5.6. The –ve sign shows the compression in crystal. In Fig:2, solid lines with open circles represent the real B1 and B2 phase, dash line represent the hypothetical B1 and B2 phase for the present study. The solid square (■) represents the experimental values of B1 and B2 phase for the present compound.

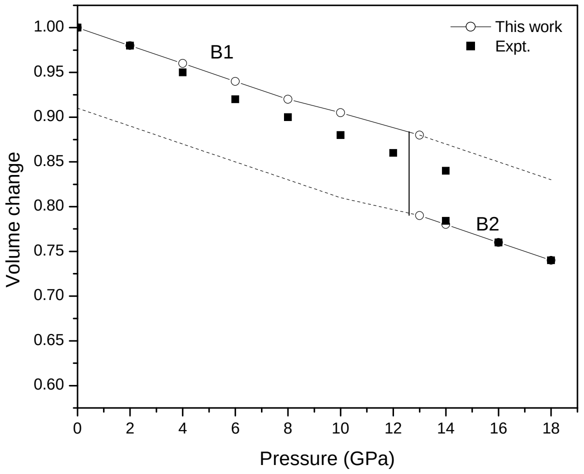

Fig: 2 Variation of volume changes V_P/V_0 with pressure for CeBi.

The study of elastic behavior under pressure is well known to supply useful information about change in the character of the covalent and ionic forces induced in the crystal as it is subjected to the phase transformation. We have calculated the second order elastic constants of the materials under study.

Table-3 Elastic constants of CeBi.

Compound	C_{11}	C_{12}	C_{44}	dB/dP
CeBi				
(Present)	102.26	21.36	11.85	5.689
(Others)	-	-	-	2.1^a

a-ref [3].

It is found that C_{11} varies largely under the effect of pressure as compared with the variations in the C_{12} and C_{44}. Since the elastic constant C_{11} represents elasticity in length. A longitudinal strain produces a change in C_{11}. The elastic constants C_{12} and C_{44} are related to the elasticity in shape, which is a shear constant. A transverse strain causes a change in shape without a change in volume. The second order elastic constants (SOEC's) and pressure derivatives of rare earth pnictide (CeBi) have been calculated by using equation (5), (6), (7) and (8) and they are given in Table-3. Our present values of SOEC's are close to available theoretical data [3]. The experimental values of second order elastic constants are not available.

An overall assessment of our results shows that the values obtained from the present potential model are in good agreement with the available experimental data [3]. Finally, we can conclude that the present potential model has successfully revealed the description of the high-pressure phase transition and allied properties of cerium bismuth compound.

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