Pressure Induced Phase Transition in Monopnictides CeSb and LaSb

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Abstract

In the present paper, monopnictides of Ce and La, which crystallize in B_1 structure, have been studied using effective interaction potential (EIP) approach. The phase transition pressure and volume collapses for CeSb and LaSb predicted from this approach are found to be close to experimental data.

Key Words: Phase transition, volume collapse, three-body potential.

1. Introduction

In recent studies, high pressure structural behavior of binary AB compounds with NaCl type structure have been a popular topic in condensed matter research. These compounds undergo first order structural phase transition from NaCl(B_1)-structure to CsCl(B_2)-structure at high pressure. These rare earth elements are trivalent and their corresponding monopnictide compounds show the lanthanide contraction and these compounds show metallic characters [1]. The Cerium pnictides CeN, CeP, CeAs , CeSb and CeBi all have peculiar properties under pressure and all of them crystallize in NaCl (B_1)-structure. These compounds undergo the first order structural phase transition from NaCl(B_1)-structure to CsCl(B_2)-structure at high pressure [2]. The isostructural phase transition under high-pressure is due to the delocalization of f-electrons [3, 4].

The high pressure electronic and structural phase transition of cerium pnictides are discussed by Svane et al. [3]. Many rare-earth monochalcogenides and monopnictides show pressure-induced transitions being either of electronic or structural origin [5]. The pressure-induced variation of the lattice constant of CeSb an d LaSb indicates a continuous electronic transition in the NaCl phase up to 10 GPa, after that first-order structural transition towards distorted CsCl-(B_2) structures occur [6]. Phase transition studies of CeSb, LaSb, PrSb and NdSb have been carried out experimentally by Hayashi et al. [7]. Structural and electronic properties of LaSb and LaBi are studied by self consistent Tight Binding Linear Muffin-tin Orbital Method (TBLMTO) [8]. Recently, Srivastava et al. [9] have studied the structural and elastic properties of CeSb with two-body potential. We have followed the method as suggested by M. P. Tosi [10] and shown good agreement by Gupta et al. [11] in case of actinide compounds. This method includes the long range Coulomb, the short range overlap repulsive interaction up to nearest neighbor ions and the van der Waals Coefficients within Slater and Kirkwood approach [12].

2.   Potential Model and Method of Calculations

An isolated phase is stable only when its free energy is at minimum for the specified thermodynamic conditions. As the pressure, or other variables acting on the system, change, the free energy changes smoothly and continuously. The stability of the particular structure is decided by the minima of the Gibbs free energy ($G = U + PV$-TS). The phase transition pressure is the pressure at which the difference in Gibbs energy of two phases becomes zero (i.e. $\Delta G = (G_{B_2}(r) - G_{B_1}(r'))$. Here U is the internal energy, which at $T = 0$ K is equivalent to the lattice energy, S in the vibration entropy at absolute temperature T. At $T = 0$ K and pressure P, the Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hypothetical) structures are given by

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} \tag{1}$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2}, \tag{2}$$

where V_{B_1} (= 2.00 r^3) and V_{B_2} (= 1.54 r^3) are the unit cell volumes for phases B_1 and B_2, respectively. The first terms in energies (1) and (2) are lattice energies for B_1 and B_2 structures and are, repectively, expressed as

$$U_{B_1}(r) = \frac{-\alpha_m z^2 e^2}{r} - [\frac{C}{r^6} + \frac{D}{r^8}] + 6b \exp[(-r)/\rho] \tag{3}$$

$$U_{B_2}(r') = \frac{-\alpha'_m z^2 e^2}{r'} - [\frac{C'}{r'^6} + \frac{D'}{r'^8}] + 8b^1 \exp[(-r^1)/\rho^1] \tag{4}$$

These lattice energies consist of long-range Coulomb energy (first terms), van der Waals interaction effect (second term) and energy due to the overlap repulsion represented by Born-Mayer type potential (last term).

The lattice energies for B_1 and B_2 structures contains $\rho(b)$ and $\rho^1(b^1)$ range (hardness) parameters, respectively, for both the phases. For B_1 phase, these parameters are calculated by employing the equilibrium conditions

$$[d(U)/dr]_{r=r0} = 0 \, and \, [d^2U/dr^2] = 9kr_0B_T. \tag{5}$$

Here, B_T is isothermal bulk modulus and $K = 2$ for B_1 phase. For B_1 phase, we have followed the most suitable Gupta et al. [11] approach. Accordingly, the value of the range parameter decreases for more compact CsCl structure up to 10% and the value of hardness parameter increases by the ratio 8/6 from B_1 phase as

$$b^1 = \frac{8}{6}b. \tag{6}$$

Here, numbers 8 and 6 are the coordinate number for the B_1 and B_2 structures, respectively. The value of the hardness parameters ρ^1 in B_2 is calculated by the minima of the Gibbs free energy whereas the interionic separation is calculated from the experimental volume collapses at the phase transition pressure.

3.   Results and Discussion

In the present paper, the structural phase transition and associated volume collapses have been studied using a simple effective interaction potential (EIP) model. The applied model for NaCl (B_1 phase) and distorted CsCl (B_2 phase), discussed in the preceding section, contain four model parameters [$\rho(b)$ and $\rho^1(b^1)$], which are given in Table 1. It is clear from the Table 1 that the hardness parameter decreases from B_1 and B_2 by about 10%, which follows the results of Gupta et al. [11] in case of actinide compounds.

Table 1. Input Crystal data and model parameters.

Input parameters			Model parameters			
Comp.	r_0(Å)	B_TGPa)	ρ (Å)	$b(10^{-19}$ J)	ρ^1 (Å)	b^1 $(10^{-19}$J)
CeSb	3.210^a	71.5 ± 3^a	0.559	1034	0.509	1379
LaSb	3.245^a	71.5 ± 3^a	0.554	1122.9	0.498	1493

[a]reference [6]

We have followed the technique of minimization of $U_{B_1}(r)$ and $U_{B_2}(r\prime)$ at different pressures in order to obtain inter ionic separation r and r$\prime$ for respective B_1 and B_2 phases. We have evaluated the corresponding $G_{B_1}(r)$ and $G_{B_2}(r\prime)$ and their respective differences $\Delta G = G_{B_1}(r) - G_{B_2}(r\prime)$. These differences ΔG have been plotted against P in Figure 1 for CeSb and LaSb. At phase transition pressure P_t, ΔG approaches zero. It is clear from Figure 2 that CeSb and LaSb both show sudden collapse in volume at phase transition pressure at around 10.5 GPa and 12.6 GPa. It is also clear from Table 2 and Figure 2 that our calculated volume collapses from TBIP model for CeSb and LaSb are 13% and 9% which are very close to the experimental values 10.2% and 10%. The experimental transition pressures of CeSb and LaSb are same. The reason for this may be that the ionic radii, inter ionic separation and bulk modules for these compounds are closer to each other.
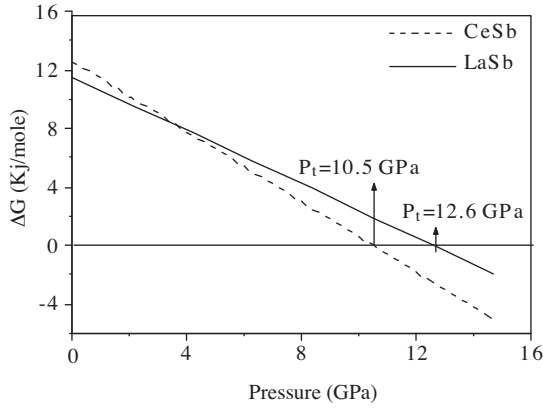
Figure 1. Variation of Gibbs free energy differences ΔG(KJ/mol) against pressure (GPa) for CeSb and LaSb.
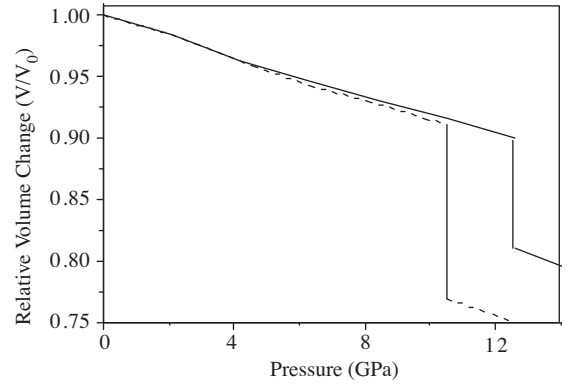
Figure 2. Variation of relative volume with pressure. The solid lines and the dashed lines are the relative volume change for the CeSb and LaSb.

Table 2. Calculated transition pressures and volume collapses.

Comp.	Transition	Transition Pressure (GPa)		Volume collapses (%)	
		Present	Experiment and others	Present	Experiment and others
CeSb	$B_1 \rightarrow B_2$	10.5	$13.6^b 11^a$	13	11^a , 10.5^b
LaSb	$B_1 \rightarrow B_2$	12.6	$8.6^C 11^a$	9	11^a 8.6^C

[a]Ref. [5][b]Ref. [9][c]Ref. [8]

From the overall study, it may be concluded that the effective interaction potential (EIP) approach is adequately suitable for the prediction of $B_1 \rightarrow B_2$ phase transition pressure and associated volume compression in case of CeSb and LaSb. The results obtained from EIP are significant because we have taken different parameters like range ρ, hardness b for the B_1 and B_2 structures in the case of CeSb and LaSb. Previous fitting potential model used same range ρ and hardness b parameters for both the B_1 and B_2 structures which is not the suitable method as suggested by Gupta et al. [11].

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