Phase Transformation and Volume Collapse of SmBi under High Pressure

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Abstract

The present study reveals the high pressure phase transition and associated volume collapse of SmBi which crystallize in NaCl (B1) structure. To achieve the goal we have used the modified three body interaction potential model (TBIPM) which is applying probably the first time for any compounds in high pressure model study. These interactions arise due to the electron shell deformation of the overlapping ions in the crystals. During phase transition there is an intermediate tetragonal phase which can be viewed as distorted CsCl (B2) structure and finally it transforms to CsCl (B2) phase. The values of phase transition pressure and associated volume collapse estimated by us are found to be well suited with experimental values. Thus our modified TBIPM is in good agreement with available measured data of SmBi.

Keywords: rare-earth compounds, phase transition, van der Waal interactions,

1. Introduction:

Despite their simple rock salt structure, the rare-earth compounds demonstrate diversities in their structural, physical and chemical properties. This is due to the presence of electron states which partially fill f shell and under pressure the nature of these f- electrons can be changed from localized to itinerant. Rare Earth monopnictides are generally semiconductors and semimetals. They demonstrate various types of magnetic ordering generally with low transition temperature. Their electronic structure and magnetic properties are sensitive to temperature, pressure and impurity effects. Most of the rare earth monopnictide compounds crystallize in cubic NaCl (B1) type structure at ambient pressure but undergo a phase transition to a CsCl (B2) structure under high pressure [1-3]. Several experimental and theoretical studies of samarium compounds have been reported. On the theoretical side, the samarium pnictides have been the subject of only few theoretical works under pressure. The previous workers have investigated the electronic structure and mechanical properties of SmBi using different methods [3, 4]. But the phase transition pressure and related volume collapse of the SmBi have not been studied theoretically, to our knowledge.

The structural properties of SmBi have been investigated recently in great detail. The salient features of SmBi were observed by J. Hayashi et al. [5] from their high-pressure x-ray diffraction experiments. They predicted that this compound crystallizes in B1 structure and the high- pressure form of the SmBi is a tetragonal structure and can be viewed as a distorted CsCl-type structure. They reported phase transition in SmBi at 18.3 GPa with the volume collapse of about 8.25%. The aim of the present work is the investigation of phase transition pressure and volume collapse of SmBi in theoretical approach. In order to achieve this goal, we have formulated a modified three-body interaction potential based on the method laid in [6-8] which consists of long range Coulombic, three body interactions, van der Waals interactions, the short range overlap repulsive forces operative up to next nearest neighbor ions, polarizablity effect and the zero point energy effect.

2. Potential model and Method of computation:

Application of pressure on crystals results in compression which leads to an increased charge transfer (or three body interaction effects) due to the deformation of the overlapping electron shells 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 interactions. Here U is the internal energy which at 0K corresponds to the cohesive energy (lattice energy), S is the vibrational entropy at absolute temperature T, pressure P and volume V. The first terms in free energy is the lattice energy in which we have included different interaction effects as given,

$$U = U_C + U_T + U_V + U_R + U_P + U_{ZPE}$$

Here, U_c is the Coulomb energy, U_T is the three-body interaction energy, U_V is the energy due to van der Waals attraction, U_R is due to the overlap repulsive forces, U_P is due to polarizability and U_{ZPE} is due to the zero point energy. At temperatures T = 0 K and pressure (P) for the real (B1) and hypothetical (B2) phases, the free energy is given by,

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

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

With $V_{B1} (= 2.00r^3)$ and $V_{B2} (=1.54r'^3)$ as the unit cell volumes for B1 and B2 phases respectively.

The first terms in equations (1) and (2) represent the lattice energies for B1 and B2 structures.

$$U_{B1}(r) = \frac{-\alpha_m Z^2 e^2}{r} - \frac{(-12\,\alpha_m Ze^2 f(r))}{r} - \left[\frac{e^2(\alpha_1 + \alpha_2)}{2r^4}\right] - \left[\frac{C}{r^6} + \frac{D}{r^8}\right] + 6b\beta_{ij}\exp[(\,r_i + r_j - r)/\rho]$$

$$6b\beta_{ii}\exp[(\,2r_i - 1.414\,r)/\rho] + 6b\beta_{jj}\exp[(\,2r_j - 1.414\,r)/\rho] + (0.5)h\langle\omega^2\rangle_{B1}^{1/2}$$

(3) and

$$U_{B2}(r') = \frac{-\alpha'_m Z^2 e^2}{r'} - \frac{(-12\,\alpha'_m Ze^2 f(r'))}{r'} - \left[\frac{e^2(\alpha_1 + \alpha_2)}{r'^4}\right] - \left[\frac{C'}{r'^6} + \frac{D'}{r'^8}\right] + 8b\beta_{ij}\exp[(\,r_i + r_j - r')/\rho]$$

$$3b\beta_{ii}\exp[(\,2r_i - 1.414\,r')/\rho] + 3b\beta_{jj}\exp[(\,2r_j - 1.414\,r')/\rho] + (0.5)h\langle\omega^2\rangle_{B2}^{1/2}$$

(4)

with α_m and α'_m as the Madelung constants for NaCl and CsCl structures, respectively. α_1 and α_2 are the electronic polarizability of cation and anion, C (C') and D (D') are the overall van der Waals coefficients of B1 (B2) phases, β_{ij} (i, j=1, 2) are the Pauling coefficients. The Ze is the ionic charge, b (ρ) are the hardness (range) parameters, r(r') are the nearest neighbour separations for NaCl (CsCl) structure, f(r) is the modified three body force parameter and r_i (r_j) are the ionic radii of ions i (j).

The other parameters include the Planck's constant, 'h' and the mean-square frequency, $\langle\omega^2\rangle^{1/2}$ which is related to Debye temperature, 'θ_D' as,

$$\langle\omega^2\rangle^{1/2} = k\theta_D/h \qquad (5)$$

In the above both equations (3) and (4) the first term is the Coulomb energy term, second is the three-body interaction energy term, third one is for polarizability, fourth term represents the energy due to van der Waals attraction, fifth term represents the overlap repulsive forces, and the last term is for zero point energy.

The overall van der Waals coefficients C and D due to dipole-dipole and dipole-quadrupole interactions are calculated from the Slater and Kirkwood variational approach [9]. The final values are obtained from the following expressions (5, 6) with the help of appropriate lattice sums S_{ij} and T_{ij} taken from Tosi [10].

$$C = c_{ij}S_{ij} + c_{ii}S_{ii} + c_{jj}S_{jj} \qquad (6)$$

$$D = d_{ij}T_{ij} + d_{ii}T_{ii} + d_{jj}T_{jj} \qquad (7)$$

For any two structures real (B1) and hypothetical (B2) at phase transition pressure (P), we have $G_{B1}(r) = G_{B2}(r')$. As an isolated phase is stable only if its free energy is at minimum, we have adopted the method of minimization of free energies for both the phases. At the phase transition pressure the difference of free energies (ΔG) approaches zero. The pressure at which $\Delta G \to 0$ is called the phase transition pressure. The associated volume with this pressure shows a sudden collapse in volume showing that the phase transition is of first order.

3. Results and Discussion:

The input crystal data and model parameters are given in Table 1. The values of three model parameters $b, \rho, f(r)$ have been determined by solving equilibrium conditions $[dU/dr]_{r=r0}= 0$ and $d^2U/dr^2=9kr_0B_T$. The table 2 explores the values of van der Waals coefficients calculated by above said Slater and Kirkwood variational approach. The phase transition pressure and volume collapse are presented in table 3. It can be noticed that the structural properties of SmBi have been predicted well from the present study. The calculated value of phase transition pressure (P_t=17.8 GPa) and volume collapse (8.41%) are in good agreement with available experimental data, (P_t=18.3 GPa) and (8.25%) respectively. The comparison has been shown in table 3.

The figure1 (a) shows the variation of difference of free energies in both phases, ΔG with pressure for SmBi. The relative volumes, $V(P)/V(0)$ (Here, $V(P)$ is the volume of the material at applied pressure P in NaCl/CsCl phase and $V(0)$ is the volume at P=0 i.e. in NaCl phase) have been computed and plotted against the pressure in figure 1(b) to get the phase diagrams and volume collapses. The figure 2 shows the variation of interatomic Sm-Bi distances in SmBi with pressure. The Sm-Bi distance in the B1 structure is 3.775 Å at ambient pressure. As this distance is lower than the sum of ionic radii of Sm and Bi (r_i=0.89 Å, r_j=1.20 Å), the bonding between Sm

and Bi can be considered with covalent character. The distance in B2 structure suddenly increases to 3.631 Å at the transition pressure 17.8 GPa.

4. Conclusion:

The present modified interaction potential model sheds more light on the structural behavior of SmBi under pressure from a theoretical platform and it is cleared that our calculated values are in good agreement with the available experimental results.

Acknowledgments

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**Table 1*:* Input crystal data and calculated model parameters of SmBi

Input Parameters						Model Parameters		
r_i (Å)	r_j (Å)	r(Å)*	B_T (GPa)*	α_1(Å^3)	α_2 (Å^3)	$b(10^{-12}ergs)$	ρ (Å)	$f(r)$
0.89	1.20	3.775	68	4.74	6.12	38085.6996	0.1750	0.0308

*Ref [5]
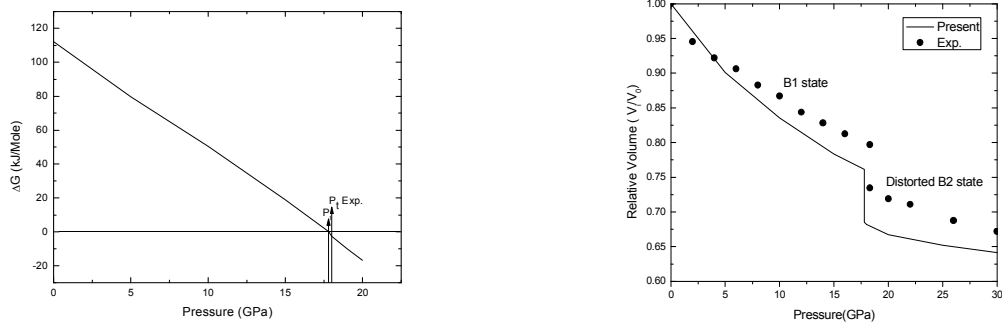
Table 2: Calculated values of van der Waals coefficients (c and d) and overall van der Waals coefficients (C in units of 10^{-60} erg cm^6 and D in units of 10^{-76} erg cm^8) for SmBi.

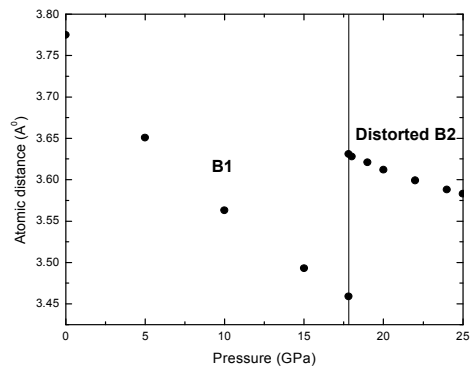| c_{ii}	c_{ij}	c_{jj}	C	d_{kk}	$d_{kk'}$	$d_{k'k'}$	D
704.16	623.48	1105.14	5746.48	1357.72	539.65	696.58	4129.37

Table 3: Calculated transition pressure and volume collapse for SmBi.

Transition pressure (GPa)		Volume collapse (%)	
Present	Expt.*	Present	Exp*
17.8	18.3	8.41	8.25

*Ref [5]

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Figure 1(a). Variation of ΔG with Pressure P (GPa)

Figure 1(b). Variation of volume change with Pressure P (GPa)

Figure 2. Variation of atomic distance with pressure of SmBi at B1 and B2 phases.

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