

Theoretical Study of Transition Pressure and Volume Collapse on Samarium Chalcogenides (SmX, X= S, Se and Te)

Dipak Raj Adhikari, Shanker Prasad Chimouriya
 Department of Natural Sciences (Physics), Kathmandu University, Nepal

Abstract: In the present paper, we have been studied the theoretical transition pressure of samarium chalcogenides by using potential model. We have reviewed bulk modulus by simple calculation. The transition pressure, volume collapse and bulk modulus predicted from this approach are found to be close to experimental data.

Key words: Samarium Chalcogenides, phase transition, transition pressure.

I. Introduction

Single crystal or polycrystal of samarium chalcogenides can be obtained experimentally by reacting the metal with sulfur, selenium or tellurium vapors at high temperature [1]. Thin films can be obtained by magnetron sputtering [2] or electron beam physical vapor deposition i.e. bombardment of samarium metal target with electrons in an appropriate gas atmosphere (e.g. hydrogen disulfide for SmS) [3]. The SmS returns to semiconducting state at lower pressure of about 0.5 kbar [1]. In SmS not only color but also other properties are changed under the effect of pressure. The band gap of samarium chalcogenides are 0.15 eV, 0.45eV and 0.65eV respectively at zero pressure [1-5]. In transition pressure (6.5 kbar for SmS) the gap is still finite and low resistivity. Samarium sulfide undergoes a discontinuous semiconductor to metal transition at appropriate pressure of 6.5kbar.

II. Theoretical Methodology

In order to understand of some properties of SmX semiconducting compounds, we made following assumption: the change in force constant is small, the short-range interactions are effective up to the second neighbor ions, and the atoms are held together with harmonic elastic without any internal strain within the crystal. In this system, all ions are not at centers of inversion symmetry and undergo internal displacements when the lattice is strained. The strain does not change the macroscopic dimension of the material but involves the transition of the anion lattice relative cation lattice. The inter-ionic potential for the compound in the framework of two body interaction potential is expressed for the SmX in either NaCl or CsCl structure is given as

$$U(r) = U_C(r) + U_{SR}(r) + U_V(r) \quad (1)$$

The first term is being the Coulomb's energy, and follows as

$$U_C(r) = - \sum_{i,j} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} = - \frac{\alpha_m Z^2 e^2}{4\pi\epsilon_0 r} \quad (2)$$

with α_m as the Madelung constant [6-8], $Z_i (Z_j)$ is the valency of cation(anion), r_{ij} is the separation distance between i and j ions, e is the electronic charge and ϵ_0 is the permittivity in free space.

The second term of eqn.(1) represents the short-range (SR) overlap repulsive energy,

$$U_{SR}(r) = \sum_{i,j} b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right)$$

$$U_{SR}(r) = n_1 b\beta_{ij} \exp\left(\frac{r_i + r_j - r}{\rho}\right) + \frac{n_2}{2} b\beta_{ii} \exp\left(\frac{2r_i - kr}{\rho}\right) + \frac{n_2}{2} b\beta_{jj} \exp\left(\frac{2r_j - kr}{\rho}\right) \quad (3)$$

Following Hafemeister and Flygare potential, k being the structure factor and β_{ij} are the Pauling coefficient defined as:

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \quad (4)$$

with $Z_i (Z_j)$ and $n_i (n_j)$ as the valency and number of outermost electrons in the cations(anion) respectively. The symbol b and ρ are being the short-range (b , hardness and ρ , range) repulsive potential parameters. The last term in eqn.(1) is the Van der Waal's (vdW) potential energy, expressed as:

$$U_V(r) = -\sum_{i,j} \frac{c_{ij}}{r_{ij}^6} - \sum_{i,j} \frac{d_{ij}}{r_{ij}^8} = -\frac{C}{r^6} - \frac{D}{r^8} \quad (5)$$

due to dipole-dipole (d-d) and dipole-quadrupole (d-q) interaction. $c_{ij} (d_{ij})$ represents the Van der Waal coefficients associated to the d-d(d-q) interactions and $C (D)$ are the corresponding overall Van der Waal coefficients defined as [6-12]

$$C = n_1 c_{ij} + \frac{n_2}{2} \frac{c_{ii} + c_{jj}}{k^6} \quad (6)$$

$$D = n_1 d_{ij} + \frac{n_2}{2} \frac{d_{ii} + d_{jj}}{k^8} \quad (7)$$

We follow the variational method (Slater and Kirkwood)[SKV Method]] [9-16] to derive c_{ij} and d_{ij} as [6]

$$c_{ij} = \frac{3}{2} \frac{e\hbar}{\sqrt{m_e}} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \alpha_i \alpha_j \left[\left(\frac{\alpha_i}{N_i} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right)^{1/2} \right]^{-1} \quad (8)$$

$$d_{ij} = \frac{27}{8} \frac{\hbar^2}{m_e} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \alpha_i \alpha_j \left[\left(\frac{\alpha_i}{N_i} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right)^{1/2} \right]^2 \times \left[\left(\frac{\alpha_i}{N_i} \right) + \frac{20}{3} \left(\frac{\alpha_i \alpha_j}{N_i N_j} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right) \right]^{-1} \quad (9)$$

where, m_e is the electron's mass, $\alpha_i (\alpha_j)$ is the electronic polarizability and $N_i (N_j)$ denotes the effective number of electrons of the cation (anion). The values of overall Van der Waal coefficients are obtained using eqns. (6) and (7)

By substituting the expressions of $U_C(r)$, $U_{SR}(r)$ and $U_V(r)$ in eq.(1) we obtain.

$$U(r) = -\frac{\alpha_m Z^2 e^2}{4\pi\epsilon_0 r} + n_1 b \beta_{ij} \exp\left(\frac{r_i + r_j - r}{\rho}\right) + \frac{n_2}{2} b \beta_{ii} \exp\left(\frac{2r_i - kr}{\rho}\right) + \frac{n_2}{2} b \beta_{jj} \exp\left(\frac{2r_j - kr}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^8} \quad (10)$$

The bulk modulus for a given material is defined as

$$B_T = -V \frac{dP}{dV} \quad (11)$$

So at equilibrium condition, i.e. at zero pressure and zero Kelvin of temperature, the eqn. (10) becomes

$$\left. \frac{d^2 U(r)}{dr^2} \right|_{r=r_0} = 9Kr_0 B_0 \quad (12)$$

The change in volume associated with the electronic transition from divalent to trivalent state [17] is given by

$$\left(\frac{\Delta V}{V_0} \right)_{elec} = \left[1 + \left(\frac{\Delta a}{a_0} \right) \right]^3 - 1 \quad (13)$$

where $\Delta a = 2(r^{+++} - r^{++}) \exp\left[-(\Delta E_g - \alpha P)/kT\right]$, r^{+++} and r^{++} are the ionic radii of the samarium ion, a_0 and ΔE_g are the lattice parameter and α is the rate at which ΔE_g close with pressure. " α " the rate at which the energy gap ΔE_g between the $4f$ level and conduction band decreases with pressure is determined

[18] such as Anderson and Nafe [19] obtained an empirical relationship between bulk modulus B_0 at atmospheric pressure and specific volume (per ion pair) V_0 of the form given by

$$B_0 \sim (V_0)^{-x} \quad (14)$$

They found for particular class of compounds where the value of x depends on the class of compounds. For chalcogenides they found x to be 1. We have investigated an empirical relationship between bulk modulus (B_0) at atmospheric pressure and specific volume V_0 given by

$$B_0 = A(V_0)^{-1} \quad (15)$$

Where A is the constant having the value 2×10^6 . The values of lattice parameters a and specific volume V_0 for samarium chalcogenides are given in table (6). Using the value of specific volume V_0 , we have calculated bulk modulus B_0 for samarium chalcogenides. The calculated values of B_0 are compared with the experimental values and are found in a reasonable agreement between them, considering the error bars in the data available [11]. Over all calculation have been done by using MATLAB.

III. Results and Discussion

The objective of the study was to understand some of the thermodynamical variables associated with phase transition at zero temperature. The model has two free parameters: the range (ρ) and hardness (b), which was estimated by the proper utilization of the equilibrium distance. Deduced values of free parameters allowed us to predict the phase transition pressure and associated volume collapse. For the computational process first of all we have collected the structure dependent parameters; Madelung constant (α_m), number of nearest neighbor ions (n_1), number of next nearest neighbor ions (n_2), crystal constants k and K for B1(NaCl) and B2(CsCl) phases and listed these values in table 1. The input data: the ionic radii of cation (r_i) and anion (r_j), equilibrium interionic separation (r_0) at zero pressure, bulk modulus (B_0) at zero pressure, electronic polarizabilities α_i (α_j) of cation(anion) of SmS, SmSe and SmTe are presented in table 2. While performing the numerical computation, we presumed that the crystals considered are purely ionic, i.e. the interionic potential depends on the electronic polarizabilities of the individual ions.

Using the polarizabilities data of table 2, we first deduce the Van der Waal coefficients from the Slater-Kirkood variation method using eqns. (8) and (9) as well as the overall Van der Waal coefficients using eqns. (6) and (7). The overall vdW coefficients of SmS, SmSe and SmTe for their B1 and B2 phases are presented in table 3. For such purposes, we have two free parameters, namely, range and hardness parameters (ρ and b). We have deduced their values from the knowledge of equilibrium distance and the bulk modulus following the

equilibrium condition $\left. \frac{dU}{dr} \right|_{r=r_0} = 0$ and eqn. (12). The values of ρ and b for SmS, SmSe and SmTe in their

B1 and B2 phases are presented in table 4. In an attempt to reveal the structural phase transition of SmS, SmSe and SmTe, we minimize the Gibb's free energies $G_{B1}(r)$ and $G_{B2}(r')$ for equilibrium interionic separation (r) and (r') for a given pressure. The Gibbs free energy difference $\Delta G = G_{B1}(r) - G_{B2}(r')$ have been plotted as function of pressure (P) in Figure 1 for SmS, Figure 2 for SmSe and Figure 3 for SmTe by using the interionic potential discussed above. The pressure corresponding to $\Delta G \rightarrow 0$ is the phase transition pressure (P_t) (indicated by arrow in figures). At zero pressure the B1 crystal phase is thermodynamically and mechanically stable, while B2 is not. As pressure increases, beyond the phase transition pressure (P_t), the B2 system becomes mechanically and thermodynamically stable. We have also calculated the fractional volume collapse in percentage during the process of phase transition. The phase transition pressure (P_t) and percentile fractional volume collapse ($\Delta V / V_0$)% are presented in table 5 along with available experimental data and obtained by other theoretical works.

This concludes that the transition is almost continuous for SmSe and SmTe. It is thus argued that the major volume discontinuity in pressure-volume phase diagram for SmS identifies the structural phase transition from NaCl to CsCl. We have also computed the value of relative volume associated with various compressions and plotted them against various pressures as shown in Figure 4 for SmS, Figure 5 for SmSe and Figure 6 for SmTe. We have also calculated the fractional volume collapse in percentage during the process of phase transition. The phase transition pressure (P_t) and percentile fractional volume collapse ($\Delta V / V_0$)% and bulk modulus are presented in table 5 and 6 along with available experimental data and obtained by other theoretical works.

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Table 1. The structure dependent input parameters: Madelung constant (α_m), number of nearest and next nearest neighbor ions (n_1) and (n_2), crystal constants (k) and (K).

Phase	α_m	n_1	n_2	k	K
B1(NaCl)	1.7475	6	12	$\sqrt{2}$	2
B2(CsCl)	1.7626	8	6	$2/\sqrt{3}$	$8/(3\sqrt{3})$

Table 2. The input parameters: ionic radius of cation (r_i), ionic radius of anion (r_j), equilibrium interionic separation (r_0), electronic polarizability of cation (α_i), electronic polarizability of anion (α_j), bulk modulus at zero pressure (B_0) for SmS, SmSe and SmTe.

Compound	$r_i(\text{\AA})$	$r_j(\text{\AA})$	$a(\text{\AA})$	$r_0(\text{\AA})$	$\alpha_i(\text{\AA}^3)$	$\alpha_j(\text{\AA}^3)$	$B_0(\text{kbar})$
SmS	1.36 ^b	1.70 ^b	5.97 ^a	4.221	28.8 ^b	2.9 ^b	476 ^a
SmSe	1.36 ^b	1.84 ^b	6.22 ^a	4.398	28.8 ^b	3.8 ^b	520 ^a
SmTe	1.36 ^b	2.07 ^b	6.60 ^a	4.662	28.8 ^b	5.5 ^b	400 ^a

^aRef [5], ^bRef [15,16]

Table 3. Calculated over all Van der Waal coefficients C and D of SmS, SmSe and SmTe for B1 and B2 phases

Compound	B1(NaCl) structure		B2(CsCl) structure	
	$C(\text{eV}\text{\AA}^6)$	$D(\text{eV}\text{\AA}^8)$	$C(\text{eV}\text{\AA}^6)$	$D(\text{eV}\text{\AA}^8)$
SmS	2904	10697	5172	18319
SmSe	3344	12605	5840	20825
SmTe	4134	16145	7030	25542

Table 4. Computed model parameters: range parameter (ρ) and hardness parameter (b) of SmS, SmSe and SmTe for B1 and B2 phases.

Compound	B1(NaCl) structure		B2(CsCl) structure	
	$\rho(\text{\AA})$	$b(\text{eV})$	$\rho(\text{\AA})$	$b(\text{eV})$
SmS	0.2237	23.6972	0.2887	5.4404
SmSe	0.6317	7.6837	0.7451	3.8292
SmTe	0.6938	6.3525	0.8075	3.2811

Table 5. The calculated values of phase transition pressure (P_t) and percentile volume collapse ($\Delta V/V_0$) for SmS, SmSe and SmTe.

Compounds	P_t (kbar)		$\Delta V/V_0$ (%)	
	Present (Potential model)	Others' works	Present (Potential model)	Others' work
SmS	6.98	6.5 ^a , 12.4 ^b , 10 ^c	11.71	13.5 ^a , 13.8 ^b , 11.1 ^c
SmSe	76.5391	40 ^a , 34 ^b , 30-90 ^c , 26-40 ^d , 33 ^e	0.27	8 ^a , 11 ^c , 7 ^d , 9.8 ^e
SmTe	60.0527	20-80 ^a , 52 ^b , 60-80 ^c , 46-75 ^d , 62 ^e	0.28	9 ^c , 7 ^d , 8.4 ^e

^aRef. [11], ^bRef. [12], ^cRef. [13], ^dRef. [14], ^eRef. [15]

Table 6. Values of lattice parameter and bulk modulus for divalent samarium chalcogenides.

Compounds	Lattice parameter (a) \AA	Specific volume (M/ρ) cm^3	Bulk modulus (B_0) kbar	
			Calc	Expt.
SmS	5.97	32.0	628	476
SmSe	6.22	35.86	556	520
SmTe	6.60	43.2	462	400

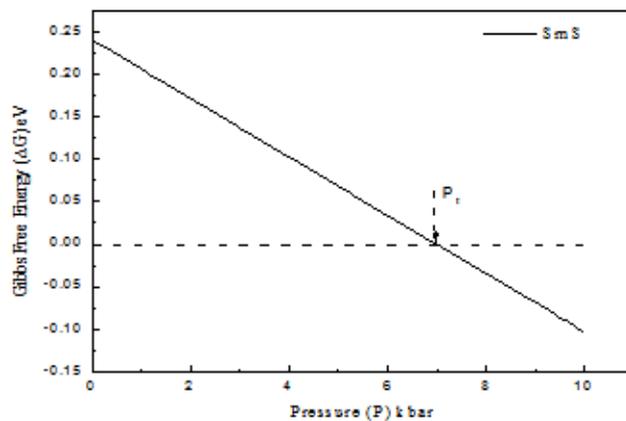


Figure 1. The variation of Gibb's free energy difference with pressure for SmS

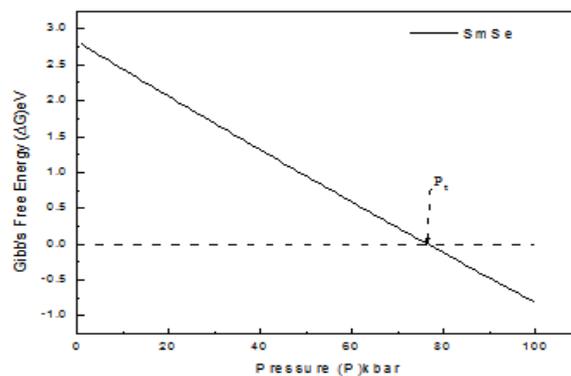


Figure 2. The variation of Gibb's free energy difference with pressure for SmSe

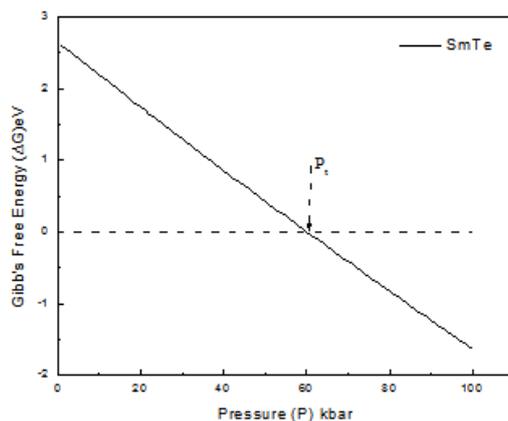


Figure 3. The variation of Gibb's free energy difference with pressure for SmTe

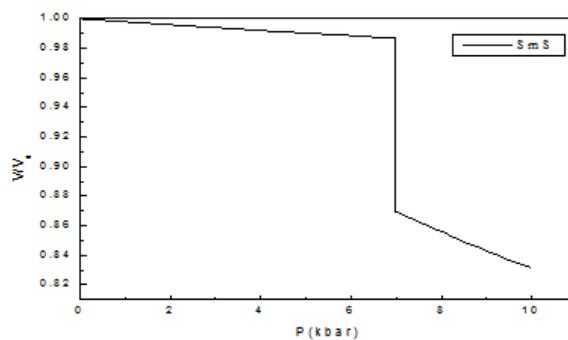


Figure 4. The variation of fractional volume with pressure for SmS

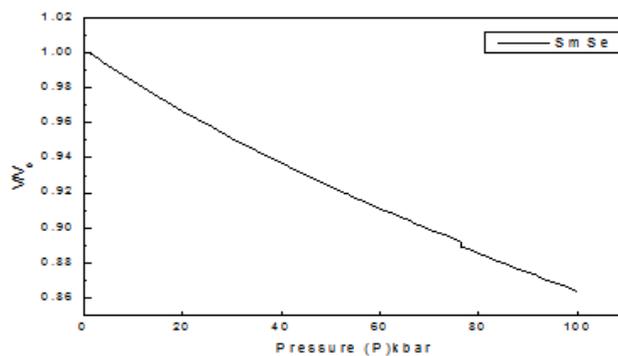


Figure 5. The variation of fractional volume with pressure for SmSe

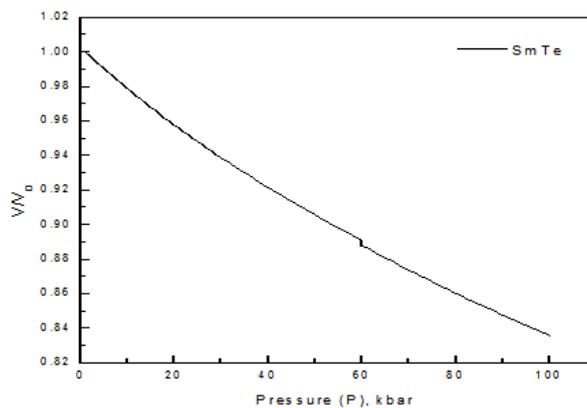


Figure 6. The variation of fractional volume with pressure for SmTe