

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

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

Abstract: A potential model is developed for determining the transition pressure of samarium chalcogenides (SmX, X= S, Se and Te). This method requires only two free parameters namely range and hardness (ρ and b) to calculate the transition pressure and volume collapse with different combination. It also provides the information on the structural changes NaCl- to CsCl.

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]. The Band gaps of samarium chalcogenides are 0.15 eV, 0.45eV and 0.65eV respectively at zero pressure [1-5]. The transition is associated with the promotion of a 4f electron in the 5d band, changing the valence from Sm²⁺ to Sm³⁺. At the high pressure collapse phase the lattice constant changes from $a = 5.97 \text{ \AA}$ to $a = 5.70 \text{ \AA}$.

II. Method of Calculation

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,

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

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

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 valence 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, α_i (α_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 eqn (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

$$B_T = -V \frac{dP}{dV}$$

But $\frac{dU}{dV} = -P$ and $\frac{d^2U}{dV^2} = -\frac{dP}{dV}$, therefore

$$B_T = V \frac{d^2U}{dV^2}$$

But

$$\frac{dU}{dV} = \frac{dU}{dr} \frac{dr}{dV}$$

And

$$\begin{aligned} \frac{d^2U}{dV^2} &= \frac{d}{dV} \left(\frac{dU}{dV} \right) = \frac{d}{dV} \left(\frac{dU}{dr} \frac{dr}{dV} \right) = \frac{d}{dV} \left(\frac{dU}{dr} \right) \frac{dr}{dV} + \frac{dU}{dr} \frac{d^2r}{dV^2} \\ &= \frac{d^2U}{dr^2} \left(\frac{dr}{dV} \right)^2 + \frac{dU}{dr} \frac{d^2r}{dV^2} \end{aligned}$$

$$\text{But } V = Kr^3, \quad \frac{dr}{dV} = \frac{1}{3Kr^2},$$

and

$$\frac{d^2r}{dV^2} = \frac{d}{dV} \left(\frac{dr}{dV} \right) = \frac{d}{dr} \left(\frac{dr}{dV} \right) \frac{dr}{dV} = \frac{d}{dr} \left(\frac{1}{3Kr^2} \right) \frac{1}{3Kr^2} = \frac{1}{3K} (-2)r^{-3} \frac{1}{3Kr^2} = -\frac{2}{9K^2r^5}$$

Therefore

$$B_T = Kr^3 \left[\frac{d^2U}{dr^2} \left(\frac{1}{3Kr^2} \right)^2 + \frac{dU}{dr} \left(-\frac{2}{9K^2r^5} \right) \right]$$

$$B_T = \frac{1}{9Kr} \frac{d^2U}{dr^2} - \frac{2}{9Kr^2} \frac{dU}{dr} \quad (11)$$

So at equilibrium condition, i.e. at zero pressure and zero Kelvin of temperature, the eqn. (11) becomes

$$\left. \frac{d^2U(r)}{dr^2} \right|_{r=r_0} = 9Kr_0B_0 \quad (12)$$

Over all calculation have been done by using MATLAB.

III. Results and discussion

The potential model is used to analyze the phase transition of samarium chalcogenides. 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. 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). 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).

We have undertaken structural properties in an ordered way. 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 Gibbs free energies $G_{B_1}(r)$ and $G_{B_2}(r')$ for equilibrium interionic separation (r) and (r') for a given pressure. The Gibbs free energy difference $\Delta G = G_{B_1}(r) - G_{B_2}(r')$ 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. Eventually, at pressure higher than the theoretical thermodynamical transition pressure, the B1 crystal becomes thermodynamically unstable while the B2 remains stable up to the greatest pressure studied 1000 kbar. 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.

The estimated value of P_t is slightly higher than those already found by experimental data. The magnitude of discontinuity in volume at transition pressure calculated from the diagram is much larger for SmS as compared those for SmSe and SmTe. 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 rock-salt to CsCl.

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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 (Å)	r_j (Å)	a (Å)	r_0 (Å)	α_i (Å ³)	α_j (Å ³)	B_0 (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 (eVÅ ⁶)	D (eVÅ ⁸)	C (eVÅ ⁶)	D (eVÅ 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 ^e	11.71	13.5 ^a , 13.8 ^b , 11.1 ^e
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]

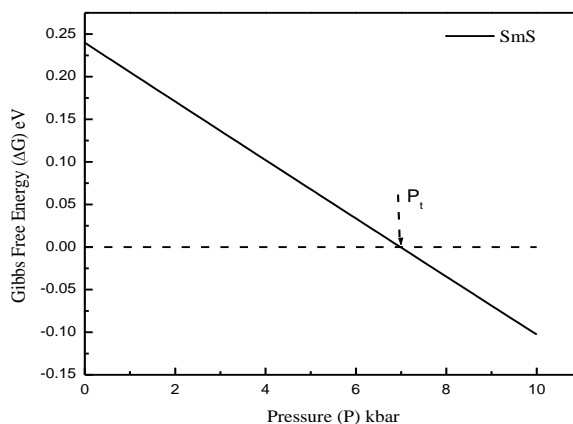


Figure 1. The variation of Gibb's free energy difference with pressure for SmS

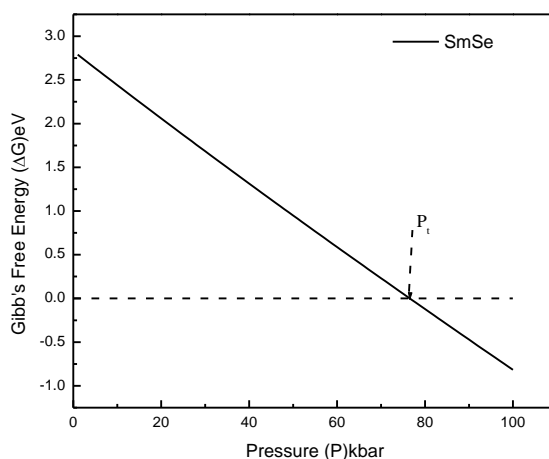


Figure 2. The variation of Gibb's free energy difference with pressure for SmSe

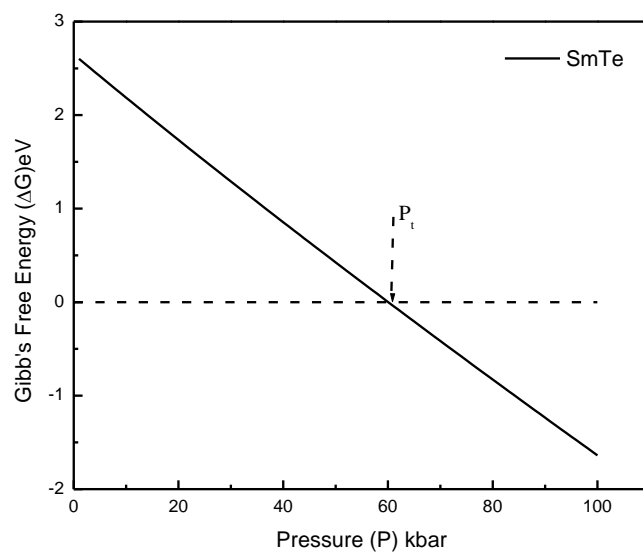


Figure 3. The variation of Gibb's free energy difference with pressure for SmTe