

9-22-2019

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Recommended Citation

Adhikari, D. Raj; Khatri, S.; Chaudhary, D. Kumar; and Lamichhane, H. Prasad (2019) "The Gibb's Free Energy and Magnetic Susceptibility of Samarium Chalcogenides (SmX, X=S, Se and Te)," *Eurasian Journal of Physics and Functional Materials*: Vol. 3: No. 3, Article 9.

DOI: <https://doi.org/10.29317/ejpfm.2019030309>

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The Gibb's Free Energy and Magnetic Susceptibility of Samarium Chalcogenides (SmX, X=S, Se and Te)

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DOI: 10.29317/ejpfm.2019030309

Received: 31.07.2019 - after revision

In the present paper, the magnetic susceptibility have been studied under the effect of pressure at constant temperature in samarium chalcogenides (SmX, X=S, Se and Te). The samarium chalcogenides have predicted the pressure induced structural and electronic transition from NaCl structure (FCC lattice) to CsCl structure (BCC lattice). The f energy level of electrons in the compounds (SmX, X=S, Se and Te) have been shifted towards 5*d* conduction band due to the influence of pressure at constant temperature. The variation of the magnetic susceptibility under the effect of pressure at constant temperature have been calculated. The calculated values and parameters are in close agreement with the experimental results.

Keywords: Gibb's free energy, magnetic susceptibility, transition pressure and samarium chalcogenides.

Introduction

The chalcogenide material containing the chalcogen element S, Se and Te have wide application in technological uses like thermo-electrics, non-linear optical materials and photoelectric. The magnetic property have been applied electronic devices and biological systems such as GMR (Gaint magneto resistance) Magnetic field Sensor and LED [1]. The SmS has used as a new kind of non-volatile memory, bulk thermoelectric material and pressure induced semiconductor to metal

transition occurred due to conversion of Sm^{2+} divalent to Sm^{3+} trivalent of samarium ion [1-6]. The rare-earth metals Sm that have the $4f^55d$ configuration. The magnetic susceptibility of Samarium chalcogenides varies under the effect of pressure at constant temperature [7]. They have used in various practical application on the field of electro-optic component, electronics, and telecommunications devices, integrated optical systems and remote sensing devices [8]. The energy band gap has reduced at high pressure [9-11]. Semiconducting state due to different lattice behavior and discontinuous transition at 6.5 kbar [12-13]. Electrical properties are equally important for the thermoelectric activity, and as such the band convergence has been extensively characterized [14-16], and the effect of thermal disorder on the band structure has been studied [17,18]. The present studies have reviewed Gibb's free energy and magnetic susceptibility under the effect of pressure at constant temperature. The calculated values are in close agreement with the experimental results.

Theoretical Calculation

The single crystal or polycrystals of Samarium chalcogenides were obtained experimentally by reacting of the metal with Sulfur, Selenium or Tellurium vapours at high temperature. The thin film was produced by magnetron sputtering or electron beam physical vapour deposition that is bombardment of Samarium metal target with electron an appropriate gas atmosphere. The band gap of Samarium chalcogenides are 0.15 eV, 0.45 eV and 0.65 eV respectively. The transition associated with promotion of $4f$ electron into the $5d$ band changing the valence from Sm^{2+} divalent to Sm^{3+} trivalent. The X-ray powder photograph conformed both the NaCl structure and lattice constant (5.97 Å) appropriate to SmX (X=S, Se and Te) [4, 19]. The SmX (X=S, Se and Te) [19] have predicted the resistance as a function of pressure at 293 ° K and abruptly decreases at 6.5 kbar pressure finally occurred the first order phase transition. The SmSe and SmTe [4, 19-21] have been shown the continuous transition type. The electronic transition from $4f^6$ level to $4f^55d$ conduction- band states occurred due to shrinking gap between the $4f$ level and bottom of the conduction band. One of the interesting aspects of Samarium chalcogenides has their magnetic susceptibility under the effect of pressure at constant temperature. The ground state of Sm^{2+} has $L=3$, $S=3$ and $J=0$ with the excited $J=1$ in the free ion. The samarium, which has the f^5d configuration, would yield a curie law from the localized f^5 moments. The magnetic susceptibility in term of band width at different pressure and constant temperature is given by the formula:

$$\chi_p(T \rightarrow 0) = \mu^2 / \Delta, \quad (1)$$

where, Δ is the effective f bandwidth brought by the hybridization. The first temperature correction is also metal-like, going as $(T/\Delta)^2$. At high temperatures the magnetic susceptibility is given by the formula:

$$\chi_p = \mu^2 / (K_B T + \Delta)^2, T \gg \Delta, \quad (2)$$

These calculations qualitatively account for the susceptibility in samarium chalcogenides. The variations of magnetic susceptibility with pressure at constant temperature are shown in Table 1, 2 and 3. The inter ionic potential for two body interaction in SmX (X=S, Se and Te) can be expressed in term of phase NaCl to CsCl structure is given by the formula:

$$U(r) = U_C(r) + U_{SR}(r) + U_V(r), \quad (3)$$

The first term is being Coulomb's energy and it is given by the formula:

$$U(r) = - \sum \frac{Z_i Z_j b^2}{4\pi \epsilon_0 r_{ij}^2}, \quad (4)$$

$$U(r) = -\alpha_m \frac{Z^2 e^2}{4\pi \epsilon_0 r}, \quad (5)$$

where α_m is the Madelung Constant, Z_i, Z_j are 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 permittivity of free space.

Table 1.

Magnetic susceptibility of SmS under the effect of pressure at constant temperature $T = 0$ K.

Pressure, kbar	$(\Delta E_g)_p$, eV	χ_p , emu/mol.
0	0.080	9.47×10^{-3}
2	0.064	11.83×10^{-3}
4	0.048	15.78×10^{-3}

Table 2.

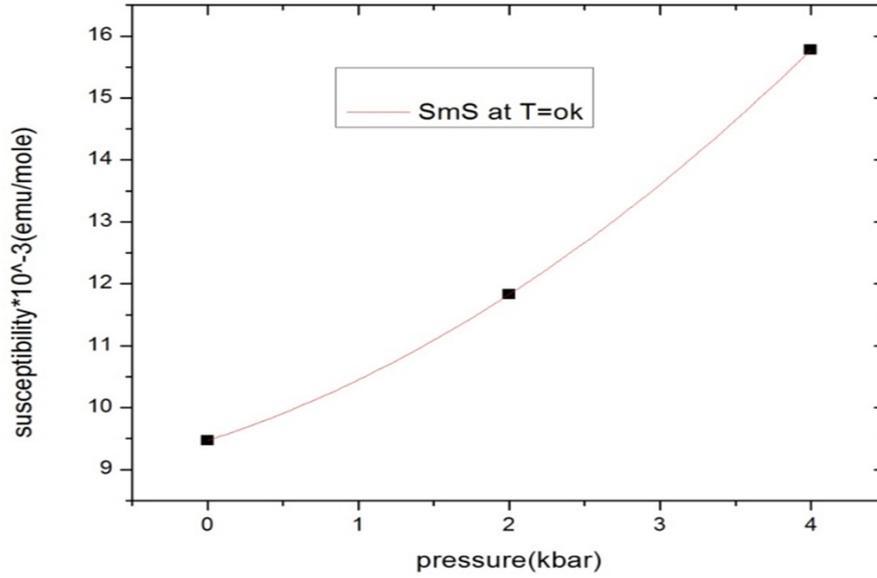
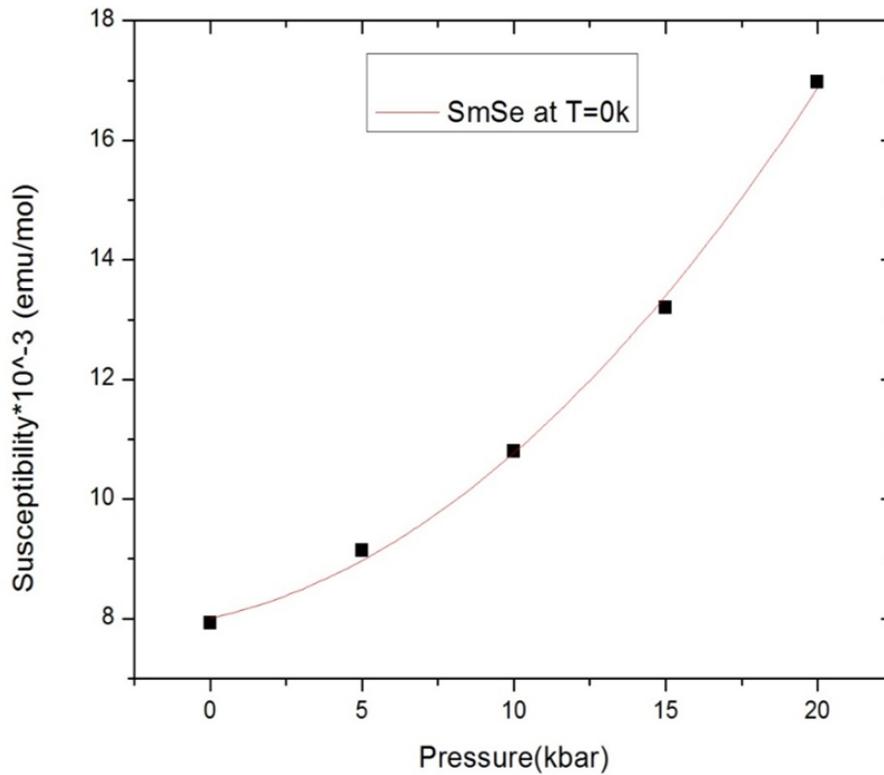
Magnetic susceptibility of SmSe under the effect of pressure at constant temperature $T = 0$ K.

Pressure, kbar	$(\Delta E_g)_p$, eV	χ_p , emu/mol
0	0.450	7.92×10^{-3}
5	0.390	9.14×10^{-3}
10	0.330	10.80×10^{-3}
15	0.270	13.20×10^{-3}
20	0.210	16.97×10^{-3}

Table 3.

Magnetic susceptibility of SmTe under the effect of pressure at temperature $T = 0$ K.

Pressure, kbar	$(\Delta E_g)_p$, eV	χ_p , emu/mol
0	0.360	7.15×10^{-3}
5	0.335	7.68×10^{-3}
10	0.310	8.30×10^{-3}
15	0.285	9.03×10^{-3}
20	0.260	9.90×10^{-3}
25	0.235	10.95×10^{-3}

Figure 1. Pressure vs magnetic susceptibility of SmS at temperature $T = 0$ K.Figure 2. Pressure vs magnetic susceptibility of SmSe at temperature $T = 0$ K.

The second term of equation (3) represents the short range force (SR) overlap repulsive energy:

$$U_{SR} = \sum_{i,j} b\beta_{i,j}e^{\left(\frac{r_i+r_j-r_{ij}}{\rho}\right)}, \quad (6)$$

$$U_{SR} = n_1\beta_{ij}e^{\left(\frac{r_i+r_j-r}{\rho}\right)} + 1/2n_2\beta_{ij}e^{\left(\frac{2r_i-kr}{\rho}\right)} + 1/2n_2\beta_{ij}e^{\left(\frac{2r_j-kr}{\rho}\right)}, \quad (7)$$

Following Hafemister and Flygare potential k being the structure factor and

β_{ij} are the pooling coefficient define as

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}, \tag{8}$$

With Z_i (Z_j) and n_i (n_j) as the valence and number if outer most electrons in the cations (anions) respectively

The symbol b and ρ are being short range (b hardness and ρ range) repulsive potential parameter. The last term in equation (3) is the vander Waals potential energy expressed as the formula:

$$U_V(r) = - \sum_{ij} \frac{c_{ij}}{r_{ij}^6} + - \sum_{ij} \frac{d_{i,j}}{r_{i,j}^8}, \tag{9}$$

$$U_V(r) = -\frac{C}{r^6} - \frac{D}{r^8}, \tag{10}$$

Due to dipole-dipole (d-d) and dipole quadrouple (d-q) interaction C_{ij} (d_{ij}) represents the Van der Waals coefficient associated to the (d-d) (d-q) interaction and $C(D)$ are corresponding overall Van der Waals coefficient defined as [22-25]

$$C = n_1 C_{ij} + \frac{n_2}{2} \frac{c_{ij} + c_{jj}}{k^6}, \tag{11}$$

$$D = n_1 d_{ij} + \frac{n_2}{2} \frac{d_{ij} + d_{jj}}{k^8}, \tag{12}$$

We follow the variational method SKV method to derive c_{ij} and d_{ij} as [22]:

$$C_{ij} = \frac{3}{2} \frac{bh}{2\pi \sqrt{m_e}} \left(\frac{1}{4\pi \epsilon_0}\right)^2 \alpha_i \alpha_j \left[\sqrt{\frac{\alpha_i}{N_i}} + \sqrt{\frac{\alpha_j}{N_j}} \right]^{-1}, \tag{13}$$

$$d_{ij} = \frac{27}{8} \frac{h^2}{4\pi^2 m_e} \left(\frac{1}{4\pi \epsilon_0}\right)^2 \alpha_i \alpha_j \left[\sqrt{\frac{\alpha_i}{N_i}} + \sqrt{\frac{\alpha_j}{N_j}} \right]^{-2} \left[\frac{\alpha_i}{N_i} + \frac{20}{3} \sqrt{\frac{\alpha_i \alpha_j}{N_i N_j}} + \frac{\alpha_j}{N_j} \right]^{-1}, \tag{14}$$

where, m_e is the mass of electron, α_i , (α_j) is the electronic polarizability, denotes the effective number of electrons of the cation (anion). The value of overall Van der Waal coefficient are obtained using substuting in equation (3) and we obtain the following:

$$U(r) = - \sum \frac{Z_i Z_j b^2}{4\pi \epsilon_0 r_{ij}} + \sum_{ij} b \beta_{i,j} e^{\left(\frac{r_i+r_j-r}{\rho}\right)} + - \sum_{ij} \frac{c_{ij}}{r_{ij}^6} + - \sum_{ij} \frac{d_{i,j}}{r_{i,j}^8}, \tag{15}$$

$$U(r) = -\alpha_m \frac{Z^2}{4\pi \epsilon_0 r} \frac{b^2}{r} + n_1 \beta_{ij} e^{\left(\frac{r_i+r_j-r}{\rho}\right)} +$$

$$+1/2n_2\beta_{ij}e^{\left(\frac{2r_i-kr}{\rho}\right)} + 1/2n_2\beta_{ij}e^{\left(\frac{2r_j-kr}{\rho}\right)} + \frac{C}{r^6} - \frac{D}{r^8}, \quad (16)$$

In transformation of Sm^{2+} to Sm^{3+} has the smaller ionic radius, lattice constant reduces and lowering the energy of the lowest $5d$ band below initial $4f$ state. The minimum value of Gibbs free energy is given by the formula:

$$G = U(r) + PV - TS, \quad (17)$$

where U is the internal energy at 0 K, S is the entropy at absolute temperature T , Pressure P and Volume V .

$$\Delta G = G_1 - G_2, \quad (18)$$

The bulk modulus for a given material is:

$$B_T = -V \frac{dP}{dV}, \quad (19)$$

At equilibrium condition zero pressure and zero kelvin temperature, then,

$$\frac{d^2u}{dr^2} \int_{r=r_0} = 9kr_0B_0, \quad (20)$$

The total energy is given by the formula:

$$E_T = E_T^0 + P(V - V_0) + E_{elastic}, \quad (21)$$

where E_T^0 is the total energy in unstrained crystal, V_0 is the volume of crystal in initial state, V is volume of strained lattice, P is the pressure and $E_{elastic}$ is the elastic energy.

Now the value of pressure P in term of total energy in unstrained crystal is given by the formula:

$$P = \left[\frac{\partial E_T^0}{\partial V} \right]_{V=V_0}, \quad (22)$$

Now the elastic energy is

$$E_{elastic} = V/2C_{ijkl} \epsilon_{ij}\epsilon_{kl}, \quad (23)$$

For two suffix notations, $E_{elastic}$ is given by the formula:

$$E_{elastic} = V/2C_{ij} \epsilon_i\epsilon_j, \quad (24)$$

$$C_{ij} = \left[\frac{1}{V_0} \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \right]_{\epsilon=0}, \quad (25)$$

The enthalpy in a samarium chalcogenide is given by the formula:

$$H \approx H_{elect} + H_{vib}^0 + H_{vib}(T) + H_{rot}(T) + H_{trans}(T) + RT, \quad (26)$$

where H_{elect} is the electronic component of enthalpy; H^0_{vib} Vibrational component of enthalpy (main State); $H_{vib}(T)$ Vibrational component of enthalpy; $H_{rot}(T)$ Rotational component of enthalpy; $H_{trans}(T)$ translational component of enthalpy; R is the Universal gas constant and T Temperature; The entropy of the samarium chalcogenides is the sum of the following component.

$$\Delta S = S_{trans} + S_{vib} + S_{elect} - nR [\ln(nN_0) - 1], \tag{27}$$

where N_0 is the Avogadro constant and N is number of moles in molecules. The Gibbs free energy of the samarium chalcogenides at given temperature T , using zero point energy and entropy of individual members of molecules reagent (A) Sm and B (S, Se and Te) is given by the formula:

$$\Delta G = H_A - H_B + \frac{1}{2} \sum_{i \in A} hv_i - \frac{1}{2} \sum_{j \in B} hv_j - T(S_{vib}^A - S_{vib}^B + S_{rot}^A - S_{rot}^B + S_{trans}^A - S_{trans}^B), \tag{28}$$

Now energy

$$\Delta E_A = E - \sum E_{el} + \sum E_{at}, \tag{29}$$

where E is the total energy, E_{el} is the energy of electron in atom that constitute the system, E_{at} is the atomization energy,

The heat capacity at constant volume is given by the formula:

$$C_{v(vib)} = C_{v(trans)} + C_{v(rot)} + C_{v(vib)}, \tag{30}$$

The vibrational component in harmonic approximation at

$$C_{v(vib)} = R \left(\frac{hc}{kt}\right)^2 \sum_i \frac{g_i v_i^2}{\left[1 - e^{-\frac{hcv_i}{kt}}\right]^2} e^{-\frac{hcv_i}{kt}}, \tag{31}$$

where g_i is the degeneration degree of i^{th} vibration.

The energy is given by the formula:

$$E(V) = E_0 + \frac{9}{16} B_0 \left[\left\{ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right\}^3 B'_0 + \left\{ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right\} \left[6 - 4 \left(\frac{V_0}{V}\right)^{\frac{2}{3}} \right] \right], \tag{32}$$

where, E_0 is minimum energy, V_0 is corresponding volume B_0 is the bulk modulus at zero pressure.

$$B'_0 = \frac{dB_0}{dP}, \tag{33}$$

then

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}} \right] \left[1 + \frac{3}{4} (B'_0 - 4) \right] \left[\left\{ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right\} \right], \tag{34}$$

The Sm^{2+} and Sm^{3+} are the magnetic configuration due to small field spilliting. Under the effect of pressure the f level approaches the Fermi surface and superconductivity appears.

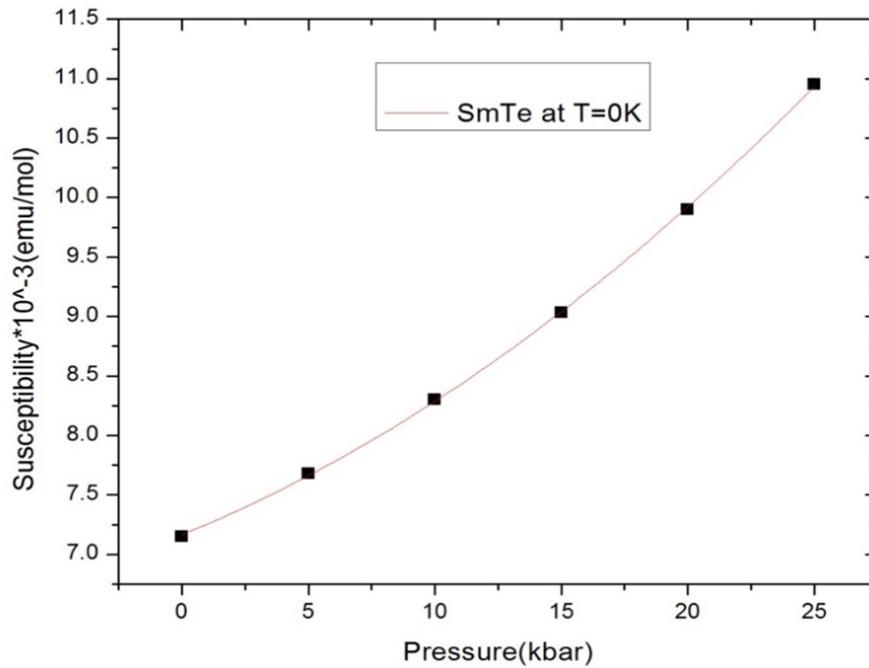


Figure 3. Pressure vs magnetic susceptibility of SmTe at temperature $T = 0$ K.

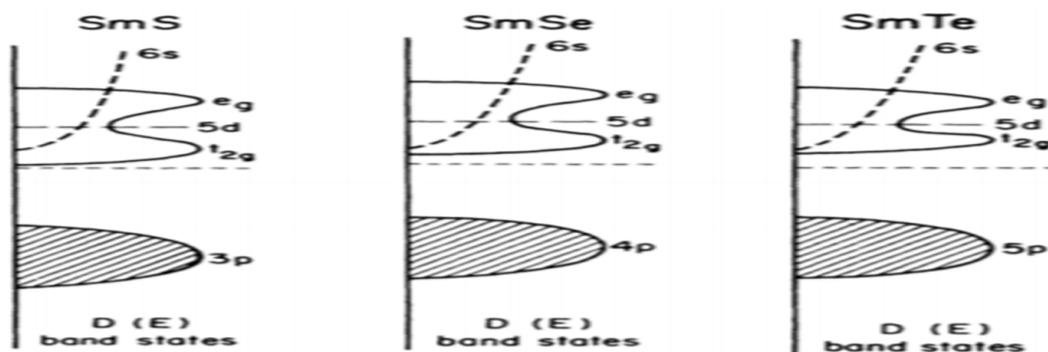


Figure 4. Energy diagram of Samarium Chalcogenides.

Results and Discussion

The simple calculation is used to analyze the magnetic susceptibility and Gibb's free energy of Samarium chalcogenides. The magnetic susceptibility under the effect of pressure at constant temperature are shown in Table 1, 2 and 3. The graph plotted between magnetic susceptibility and Pressure at constant temperature of the studied samarium chalcogenides are predicted in Figure 1, Figure 2 and Figure 3. The energy band diagram of these samarium chalcogenides are shown in Figure 4. The value of pressure increased the valence band shifted towards conduction band state, which predicted the semiconducting to metallic behavior. At high pressure and temperature the valence band acted as the conduction band. The studied compound undergoes the pressure induced structural transition from NaCl(FCC) to CsCl(BCC). The X-ray powder photograph conformed both the NaCl to CsCl structure. The SmX (X=S, Se and Te) compounds reveals the resistance as a function of pressure at 293 ° K and the resistance abruptly decreases at 6.5 kbar pressure as the first order phase transition finally occurs. The SmSe and SmTe

demonstrate the continuous transition.

Table 4.

Transition pressure (P_t), volume collapse (V/V_0), specific volume M/ρ for SmS, SmSe and SmTe.

Compound	P_t calc.	P_t exp.	V/V_0	V/V_0	M/ρ
SmS	6.98	6.5	11.71	13.5	32.0
SmSe	76.53	30-90	0.27	-	35.8
SmTe	60.05	46-75	0.28	-	43.2

In this phenomenon, the f energy level of (SmX, X=S, Se and Te) have been shifted towards $5d$ conduction band under the influence of pressure at constant temperature. The transition pressure (P_t), volume collapse (V/V_0) and specific volume M/ρ for SmS, SmSe and SmTe are shown in Table 4. The inter ionic potential for two body interaction in SmX (X=S, Se and Te) can be expressed in term of phase NaCl (FCC) to CsCl(BCC) structure and structural transition have been appeared. The electronic transition from $4f^6$ level to $4f^55d$ conduction-band states is occurred due to shrinking gap between the $4f$ level and bottom of the conduction band.

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