Jordan Journal of Physics

ARTICLE

Activation Energy and Magnetic Susceptibility of Samarium Sulfide (SmS) under the Effect of Pressure at Constant Temperature

Dipak Raj Adhikari

Central Department of Physical and Mathematical Sciences, Graduate School of Science and Technology, Mid-West University, Birendranagar, Surkhet, Nepal.

Abstract: The present paper addresses the activation energy and magnetic susceptibility in samarium sulfide (SmS) under the influence of pressure at constant temperature. The samarium sulfide has shown the pressure-induced NaCl (B1) to CsCl (B2) structural phase transition. In this transition, 4f energy level (valence band) of samarium sulfide has shifted towards the 5d conduction band within the band gap. The calculated values of magnetic susceptibility, activation energy and energy-band gap are in close agreement with the experimental results.

Keywords: Activation energy, Magnetic susceptibility, Samarium sulfide.

Introduction

The $Sm^{2+}S$ is a pressure-sensitive semiconductor. It has larger lattice constant. SmS is stable in the polycrystalline state. In SmS, the $4f^{n-1}$ state consists of three multiplets $4f^{5}(^{6}H_{J}, {}^{6}F_{J}, {}^{6}P_{J})$ for a $4f^{6}$ to $4f^{5}5d$ transition under the influence of pressure. The samarium sulfide material containing the chalcogen element S has wide applications in technological uses, like non-linear optical materials and photoelectricity. The magnetic properties of SmS have been applied in electronic devices and biological systems, such as GMR (gaint magneto-resistance), magnetic field sensors and LEDs [1]. SmS also has been used as a new kind of non-volatile memory and bulk thermoelectric materials [1-6]. The energy-band gap and magnetic susceptibility of samarium sulfide have changed under the influence of pressure at constant temperature due to 6s electron of Sm atoms involved in bonding with sulpher (S) anion [7]. SmS has been used in various practical applications and recent developments in the field of electro-optic components, electronics and telecommunication devices, as well as in integrated optical systems and remote sensing devices [8]. The energy-band gap has reduced at high pressure [9-11]. SmS has experienced discontinuous phase transition at 6.5 kbar [12, 13] under the influence of pressure. The effects of thermal disorder and band structure have been studied [14-17]. The present study aimed to provide and update the energy-band gap, activation energy and magnetic susceptibility under the influence of pressure at constant temperature. The calculated values are in close agreement with the experimental results.

Theoretical Calculation

The single crystal of poly-crystalline state of samarium sulfide was obtained experimentally by reacting the metal with sulpher vapours at high temperature. The thin film was obtained by magnetron sputtering or electron beam physical vapour deposition, where a samarium metal target was hit with electrons in an appropriate gas atmosphere. The transition associated with promotion of *4f* electron into the *5d* band changes the valence from Sm^{2+} divalent to Sm^{3+} trivalent. The X-ray powder photograph

confirmed both the NaCl structure and the lattice constant (5.97Å) appropriate to SmS [4, 18]. An interesting aspect of samarium sulfide is its magnetic susceptibility under the effect of pressure at constant temperature. The magnetic susceptibility in term of band width at different pressures and constant temperature is given by:

$$\chi_{SmS}(T \to 0) = \mu^2/\Delta \tag{1}$$

where Δ is the effective f band width brought by hybridization. At high temperatures, the magnetic susceptibility is given by:

$$\chi_{SmS} = \mu^2/(k_BT+\Delta), \quad T \gg \Delta . \tag{2}$$

The variation of magnetic susceptibility is given by :

$$\chi_{SmS} = 8N\mu^2/E_{SmS}(T) , \tag{3}$$

where $E_{SmS}(T)$ is the temperature-dependent band gap of samarium sulfide (SmS) and N is the spin density.

The carrier effective mass is given by:

$$m_{SmS}^* = 1.3 m_{SmS} , \tag{4}$$

where m_{SmS} is the mass of an electron at ambient temperature.

SmS has the NaCl (B1) structure with semiconducting behavior at low temperatures and zero pressure. In metallic phase CsCl (B2), the volume of SmS has collapsed [3, 19, 20]. The variation of activation energy of samarium sulfide at different pressures is given by:

$$(\Delta E_g{}^{SmS})_p = \Delta E_g{}^{SmS} - \alpha_{SmS}P , \tag{5}$$

where ΔE_g is the activation energy at ambient temperature and P is the pressure at which activation energy is calculated and α_{SmS} is given by:

$$\alpha_{SmS} = \frac{d(\Delta E_g{}^{SmS})}{dP} . \tag{6}$$

These calculations are fitted for the magnetic susceptibility in samarium chalcogenides. The variations of activation energy and magnetic susceptibility with pressure at constant temperature are shown in Table 1 and Table 2, respectively.

TABLE 1. Activation energy of samarium sulfide (SmS) at different pressures.

Compound	Pressure (kbar)	$(\Delta E_g{}^{SmS})$ Calc. eV	$(\Delta E_g{}^{SmS})$ Exp. eV	α_{SmS} eV $(kbar)^{-1}$
SmS	0	0.080	0.080	
	2	0.064	0.060	0.008
	4	0.048	0.030	

TABLE 2. Magnetic susceptibility of SmS under different pressures at constant temperature T = 50K.

Pressure (kbar)	$(\Delta E_g{}^{SmS})_p$ eV	$(\chi_{SmS})_p$ emu/mol.
0	0.080	8.98×10^{-3}
2	0.064	11.09×10^{-3}
4	0.048	14.48×10^{-3}

The inter ionic potential for two-body interaction in SmS can be expressed in terms of phase NaCl (B1) to CsCl (B2) structure, given by:

$$U^{SmS}(R) = U_C{}^{SmS}(R) + U_{SR}{}^{SmS}(R) + U_V{}^{SmS}(R). \tag{7}$$

The first term is Coulomb's energy and is given by:

$$U_C{}^{SmS}(R) = -\sum \frac{Z_i}{4\pi} \frac{Z_j}{\epsilon_0} \frac{e^2}{R_{ij}} \tag{8}$$

$$U_C{}^{SmS}(R) = -\alpha_m \frac{Z^2}{4\pi} \frac{e^2}{\epsilon_0 R} \tag{9}$$

where:

α_m is the Madelung constant.

Z_i, Z_j is the valency of cations (anions).

R_{ij} is the separation distance between i and j ions.

e is the electronic charge and ϵ_0 is permittivity of free space.

The second term in Eq. (7) represents the short-range force (SR) overlap repulsive energy and is given by:

$$U_{SR}{}^{SmS} = \sum_{i,j} b_h \, \beta_{ij} \, e^{\left(\frac{R_i+R_j-R_{ij}}{\rho_r}\right)} \tag{10}$$

$$U_{SR}{}^{SmS} = n_1 \beta_{ij} e^{\left(\frac{R_i+R_j-R}{\rho_r}\right)} + 1/$$
$$2n_2 \beta_{ij} e^{\left(\frac{2R_i-kR}{\rho_r}\right)} + 1/2n_2\beta_{ij} e^{\left(\frac{2R_j-kR}{\rho_r}\right)} \tag{11}$$

Hafemister and Flygare potential k is the structure factor and β_{ij} is the pouling coefficient, which is given by:

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}, \tag{12}$$

where Z_i and (Z_j) are the valence; n_i and (n_j) are the number of outer-most electrons in the cations (anions), respectively.

The symbols b_h and ρ_r are being short-range (b_h hardness and ρ_r range) repulsive potential parameters. The last term in Eq. (7) is the van der Waals potential energy expressed as:

$$U_V{}^{SmS}(R) = -\sum_{i,j} \frac{C_{i,j}}{R_{ij}^6} - \sum_{i,j} \frac{D_{i,j}}{R_{ij}^8} \tag{13}$$

$$U_V{}^{SmS}(R) = -\frac{X}{R^6} - \frac{Y}{R^8} \tag{14}$$

Interaction $C_{ij}(d_{ij})$ represents the van der Waals coefficient associated to the (d-d) (d-q) interaction and C(D) are the corresponding overall van der Waals coefficients defined as [19-22]:

$$X = n_1 C_{ij} + \frac{n_2}{2} \frac{C_{ij+}C_{jj}}{k^6} \tag{15}$$

$$Y = n_1 D_{ij} + \frac{n_2}{2} \frac{D_{ij+}D_{jj}}{k^8} . \tag{16}$$

We follow the variational method (SKV method) to derive C_{ij} and D_{ij} as [19]:

$$C_{ij} = \frac{3}{2} \frac{e\,h}{2\pi\sqrt{m_e}} \left(\frac{1}{4\pi\epsilon_0}\right)^2 \alpha_i \alpha_j \left[\sqrt{\frac{\alpha_i}{N_i}} + \sqrt{\frac{\alpha_j}{N_j}}\right]^{-1} \tag{17}$$

$$D_{ij} = \frac{27}{8} \frac{h^2}{4\pi^2 m_e} \left(\frac{1}{4\pi\epsilon_0}\right)^2 \alpha_i \alpha_j \left[\sqrt{\frac{\alpha_i}{N_i}} + \sqrt{\frac{\alpha_j}{N_j}}\right]^{-2} \left[\frac{\alpha_i}{N_i} + \frac{20}{3}\sqrt{\frac{\alpha_i \alpha_j}{N_i N_j}} + \frac{\alpha_j}{N_j}\right]^{-1} \tag{18}$$

where m_e is the mass of electron and α_i and (α_j) represent the electronic polarizability.

The values of overall van der Waal coefficient are obtained using substuting in Eq. (7); hence, we obtain:

$$U^{SmS}(R) = \sum \frac{Z_i}{4\pi} \frac{Z_j}{\epsilon_0} \frac{e^2}{R_{ij}} + \sum_{i,j} b_h \beta_{ij} e^{\left(\frac{R_i + R_j - R_{ij}}{\rho_r}\right)} + -\sum_{i,j} \frac{C_{ij}}{R_{ij}^6} - \sum_{i,j} \frac{D_{ij}}{R_{ij}^8} \tag{19}$$

$$U^{SmS}(R) = -\frac{Z^2}{4\pi} \frac{e^2}{\epsilon_0 R} + n_1 \beta_{ij} + \frac{1}{2n_2\beta_{ij}e^{\left(\frac{2R_i - kR}{\rho_r}\right)}} + 1/$$

$$2n_2\beta_{ij}e^{\left(\frac{2R_j - kR}{\rho_r}\right)} + -\frac{X}{R^6} - \frac{Y}{R^8} \tag{20}$$

The minimum value of Gibbs free energy of (SmS) is given by:

$$G_{SmS} = U^{SmS}(R) + (PV)_{SmS} - (TS)_{SmS} , \tag{21}$$

where $U^{SmS}(R)$ is the internal energy at 0K and S is the entropy at absolute temperature T, pressure **P and volume V.**

$$(\Delta G_{SmS}) = G_1 - G_2 . \tag{22}$$

The Gibbs free energy of samarium chalcogenides at temperature T, in terms of Sm and S, is given by:

$$(\Delta G_{SmS}) = H_{Sm} - H_S + \frac{1}{2}\sum_{i\varepsilon Sm} h\nu_i - \frac{1}{2}\sum_{j\varepsilon S} h\nu_j - T\left(S_{VIB}^{Sm} - S_{VIB}^{S} + S_{ROT}^{Sm} - S_{ROT}^{S} + S_{TRANS}^{Sm} - S_{TRANS}^{S}\right) . \tag{23}$$

The magnetic transition occurred in SmS under the effect of pressure at constant temperature.

Results and Discussion

The calculations have aimed to analyze and updat the magnetic susceptibility and activation energy of samarium sulfide under the effect of pressure at constant temperature. The activation energy and magnetic susceptibility of SmS are shown in Table 1 and Table 2, respectively. The graphs of activation energy with pressure and magnetic susceptibility with pressure at constant temperature of samarium sulfide are shown in Fig. 1 and Fig. 2, respectively. The pressure increased the *f* valence band shifted towards *5d* conduction band state and predicted the semiconducting to metallic behavior under the influence of pressure. At high pressure and temperature, the *f* valence band acted as the conduction band. Eqs. (1) and (2) provided the relation of magnetic susceptibility with energy-band gap. Energy-band gap decreases with increase in pressure and *vice versa* in susceptibility. The inter-ionic potential for two-body interaction in SmS can be expressed in terms of phase NaCl (B1) to CsCl(B2) structure as given by Eq. (7). Eqs. (7) to (20) give the potential energy under different parameters and conditions of a given compound. Eqs. (21) and (22) give the Gibb's free energy. Finally, the estimation based on electronic transition from *4f⁶* level to *4f⁵5d* conduction-band states occurred due to shrinking gap between the *4f* level and the *5d* bottom of the conduction band.
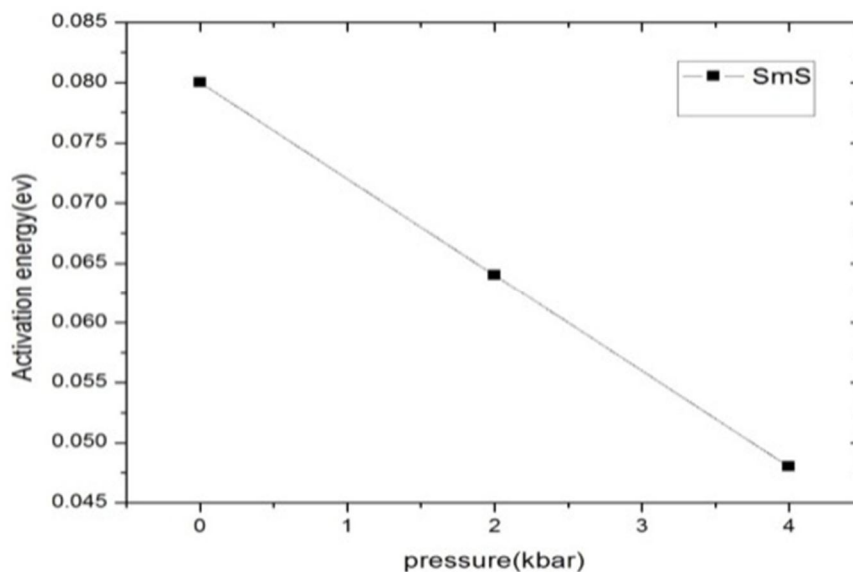
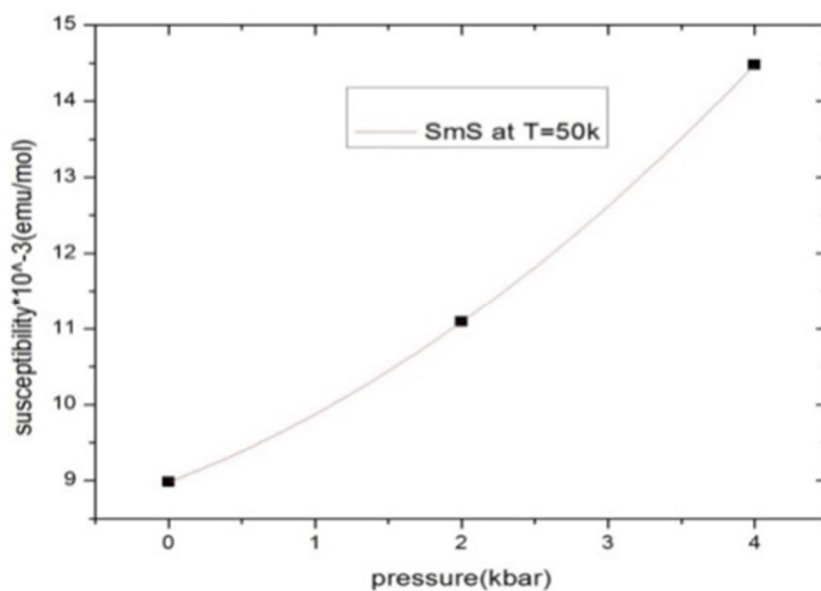FIG. 1. Activation energy with pressure for SmS.

FIG. 2. Magnetic susceptibility *vs*. pressure for SmS at temperature T = 50K.

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