Study of Transition Pressure and Nanoparticle Size in Samarium Chalcogenides [Smx (X=S, Se and Te)]

Dipak Raj Adhikari

Department of Physics, Amrit Science Campus, Tribhuvan University, Nepal

Abstract: *The pressure volume relationship for samarium chalcogenides have been obtained from high pressure X-ray diffraction studies to nearly 300 kbar. An insulator to metal transition occurred due to an f^{n-1} atomic configuration and promoted an f electron to a d - state. In this situation the density of d electron is small compare to f state. The pressure volume behavior occurred due to promotion of 4f electron in to 6s-5d conduction band, in this method, the transition pressure, and nanoparticle size of SmX (X=S,Se and Te) are calculated .The calculated values are compared with experimental results.*

I. Introduction

The magnetic nanoparticles have been applied electronic devices [1] and biological systems [2] such as GMR { (Gaint magneto resistance)Magnetic field Sensor} and LED. The synthesis and characterization of nanoparticles in search for a luminescent material [3-9]. The SmS is used as a new kind of non-volatile memory and pressure induced semiconductor to metal transition occurred due to conversion of Sm^{2+} to Sm^{3+} (divalent to trivalent) of samarium ion[10-14].The x-ray powder photograph conformed both the NaCl structure and lattice constant (5.97Å) appropriate to SmX (X=S,Se and Te)[14].The SmX (X=S,Se and Te)[13]predicted the resistance as a function of pressure at 293^0K and abruptly decreases at 6.5kbar pressure finally occurred the first order phase transition. The SmSe and SmTe [13-17] have shown the continuous transition. The resistivity decreases in the pressure range of 0-60 kbar. From optical absorption data (0.63 eV for SmTe and 0.46 eV for SmSe).The electronic transition from $4f^6$ level to $4f^5 5d$ conduction- band states occurred due to shrinking gap between the 4f level and bottom of the conduction band. The metallic conductivity at high pressure due to delocalization of 4f electron conversion of Sm^{2+} to Sm^{3+} .The metallic resistivity observed in SmSe and SmTe. In this case, the number of electron in the conduction band is the function of temperature and pressure.

II. Theoretical Methodology

A simple model is developed for determining the transition pressure. ΔE_p and nano particle size of samarium chalcogenides SmX (X=S,Se and Te) are calculated. From the pressure volume relationship, the theory of phase transition and analyzed energy as a function of average number of s-d electron per atom and the average volume per atom V. The energy is the sum of electronic and lattice is given by

$$E(V,Z)=E_e(V,Z)+E_l(V,Z) \qquad (1)$$

Where, E_e be the energy due to electronic and E_l be the energy due to lattice,Both energy are the function of (V,Z)

The volume depends on the valance of samarium ion. In fact the density of d state electron is small compare to the f-state electron in which large amount of energy is require to create a new $f^{n-1}d$ state. The microscopic derivation of this picture has been given by Verm and Heine [16].In this case the number of electrons n in the conduction band is the function of temperature and pressure then energy gap between the 4f level to conduction band. The energy gap with pressure is given by,

$$\Delta E_p=\Delta E_g - J_{ex}\, n \qquad (2)$$

Where, ΔE_g be the energy gap at zero pressure, J_{ex} be the electron hole exchange interaction and exchange parameter J_{ex} is given by

$$J_{ex} = \frac{Cd^2}{\Delta E_g^2} \qquad (3)$$

Where, C be the function of intra-atomic exchange (4f to 5d conduction band exchange), d be the orbital overlap, J_{ex} be the exchange interaction is zero for SmX (X=S,Se and Te) in semiconducting phase and n be the number of electrons in conduction band.The energy gap between conduction band and valence band with pressure is given by

$$\Delta E_p=\Delta E_g-\alpha P \qquad (4)$$

Where, ΔE_g be the energy gap at zero pressure, α be the shrinking of energy gap with pressure, it can be determined experimentally [10].The calculated and experimental value of pressure dependent energy gap are shown in table 1.The value of α related with pressure resistivity is given by,

$$\alpha = kT\frac{d\ln\rho}{dP} \quad\quad\quad (5)$$

From pressure resistivity data, the related work of electronic and lattice energy have been done by Hirst [17]. The lattice contribution energy is

$$E_l = B(V)\frac{(V-V_0)^2}{2V_0} \quad\quad\quad (6)$$

Where, V_0 be the equilibrium volume, Now the variation of bmulk modulus on the volume ,The bulk modulus on the volume [19] is given by,

$$B(V^{'})=B(V)(\frac{V}{V^{'}})^{\gamma} \quad\quad\quad (7)$$

Where, $\gamma=1.3$

The interaction energy is always attractive if the lattice is purely harmonic leading to the contraction lattice .The non- harmonic term can make the repulsive contribution to the interaction energy [18]. One electron is contributed to $E_l(V,Z)$ of the promotion of E_g from the f level to the conduction band and the binding energy E_B.The $E_l(V,Z)$ can be expressed in term of promotion of energy E_g and the lattice energy is given by

$$E_l(V,Z)=Z[E_g(V)\ \theta(E_g)+E_B]+E_{ex} \quad\quad\quad (8)$$

Where $\theta(E_g)=1$ for $E_g(V)>0$ (i.e bottom of the conduction band and above the f level) and $\theta(E_g)=0$ for $E_g(V)<0$,we have assumed that the decrease in E_g in with derease in volume [6] is given by

$$E_g(V)= E_g(V^{'})[1+\beta\frac{V-V^{'}}{V}]^{-5/3} \quad\quad\quad (9)$$

Where, $\beta$is the coefficient, it is adjusted by comparing the linear term with experimentally observed result. The variation of d-electron band width $W(V)$ is taken to be

$$W(V)= W(V^{'})[\frac{V}{V^{'}}]^{5/3} \quad\quad\quad (10)$$

The Band energy E_B is given by the relation

$$E_B= \frac{3}{5}[\frac{3}{\pi}]^{2/3}W(V)\ Z^{2/3} \quad\quad\quad (11)$$

The total electronic energy calculated by using the chemical potential for conduction electron. The total energy is the function of average fraction valence Z and volume. In equilibrium condition

$$\frac{\partial E(Z,V)}{\partial V} = 0 \ \text{for } Z > 0 \quad\quad\quad (12)$$

The second derivative must be positive

$$\frac{\partial^2 E(Z,V)}{\partial V^2} = 0 \ \text{for } Z > 0 \quad\quad\quad (13)$$

Then, the condition

$$\frac{dP}{dV}=\frac{\partial^2 E(Z,V)}{\partial V^2} - \frac{\frac{\partial^2 E}{\partial Z\partial V}}{\frac{\partial^2 E}{\partial Z^2}} >0 \quad\quad\quad (14)$$

The calculations have been done numerically. The finite value of Z shows the even transition in SmS due to $Z^{5/3}$ contribution of binding energy. The phase transition is to be expected at higher pressure in this material near the point when the bottom of the s-d band is far enough below the f band and it can be accommodate one electron per atom .The deformation potential can be calculated using the following formula [19-20].

$$\sum = \frac{E_p}{[\frac{V}{V_0}-1]} \quad\quad\quad (15)$$

Where, $\frac{V}{V_0}$ is the fraction of volume as the transition starts, again we have the relation,

$$\frac{\partial E_p}{\partial P}=\frac{\sum}{B_0} \quad\quad\quad (16)$$

With the help of $\frac{\sum}{B_0}$, the value of $\frac{\partial E_p}{\partial P}$ can be calculated. In fig 1.the pressure volume relation relationship and transition pressure are shown. Using table 2.the value of transition pressure can be calculated. The calculated transition pressure and experimental results [21] are shown and compared in Table 3.The another part of this paper SmX (X=S,Se and Te) are pressure dependent semiconductor .The particle size of SmX (X=S,Se and Te) have been calculated by effective mass of holes and electron. Now carrier effective mass of hole is given by

$$m_h^* = 1.44\ m_e^* \quad\quad\quad (17)$$

Where, m_e^* be the carrier effective mass of electron, The carrier effective mass and energy gap at zero pressure are shown in table 1. Generally electron in conduction band and holes in valence band is confined spatially. Finally both electron and holes achieved the lowest energy of an optical transition from valence band to conduction band. The expression for the radius of nanoparticle is given by

$$R^2 = \frac{h^2}{8(\Delta E_g - \Delta E_p)}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] \qquad (18)$$

Where, ΔE_p be the energy gap at zero pressure. The calculated different parameters are close agreement with the experimental results.

III. Conclusions

The pressure volume studies have been helped to understand and established the pressure induced semiconductor to metal transition in samarium chalcogenides. In this paper the values of transition pressure and nanoparticle size of SmX (X=S,Se and Te) have been calculated. The transition pressure and nanoparticle size are listed in table 2 and 3respectively. The plotted the graph P Vs $\frac{V}{V_0}$ is the similar trend to the experimental results.The transition pressure and nano particle size played the major role in theory of phase transition in samarium chalcogenides.

Table.1. The value of nanoparticle size, calculated and Experimental energy gap at zero pressure

Compound	Nanoparticle size nm	ΔE_g (P=0,eV Exp.)	ΔE_g (P=0,eV Calc.)
SmS	1.701	0.1	0.083
SmSe	4.51	0.5	0.452
SmTe	1.741	0.7	0.368

Table.2. The value of bulk modulus, energy gap at zero pressure and carrier effective mass of electron

Compound	B_0 (Kbar)	γ	ΔE_g (P=0,eV)	m_e^* (10^{-31} Kg)
SmS	476	1.3	0.1	1.437
SmSe	520	1.3	0.5	4.794
SmTe	400	1.3	0.7	4.618

Table.3. The value nanoparticle size and calculated and Experimental value of transition pressure.

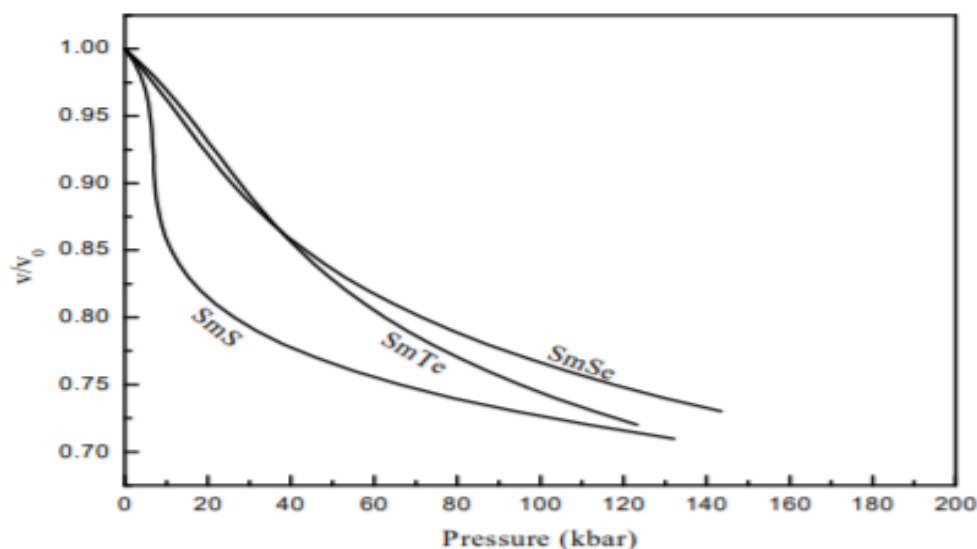| Compound	Transition Pressure Present Work- Other work		Nano particle size			
SmS 40[a],33[b]	8.06 4.51nm	6.5[a],10[b] SmTe	20-57	1.701nm 20-80[a] 62[b]	SmSe 1.741nm	20-60

[a][20],[b][21]

Fig.1. pressure Vs v/v_0 of SmX (X=S,Se and Te)

References

[1]. D.D Awschalom,M.E Flattle,N.Samarth,Sci.Am,**286(6),**66-73,2002
[2]. P.Gould; Matter today,**7**(2),36,2004
[3]. S.Thongchant,Y.Hasegawa,Y Wada,S.Yanagida,Chem.Lett.**12**,1274,2001
[4]. Y.Hesegawa,S.Tonychant,Y.Wada,H.Tanka,T Kawai,T.Sakata,H.Mori,S. Yanagida,Angwe Chem.Int Ed.**41** (12)2073-2075,2002
[5]. Y.Hasegawa,S.Tongchant,T.Kataoka,Y.Wada ,T.Yatsuhashi,N.Nakshima,S.Yangida Chem.Lett. **32**(8) 706-709,2003
[6]. S.Tongchant ,Y.Hasegawa,Y.Wada ,S.Yangida,J.Phys.Chem.**B,**107,2193,2003

[7].   M.R.Regulacio, N. Tomson,S.L.Stoll.Chem.Matter, **17**,3451(2005)
[8].   T.Mirkovic,M Hines,P.Nair,G Seholes ,Chem Matter,**17,**3451,2005
[9].   P.Wachter CRC Crit.Rev.Solid State Sci,**3**,189,1972
[10].   A. Chatterjee, A. K. Singh and A. Jayaraman, Phys. Rev. **B6**, 2285 (1972)
[11].   F. J. Reid, L. K. Matson, J. F. Miller and R. C. Himes, J. Phys. Chem. Solids **25**, 969 (1964).
[12].   R. Didchenic and F. P. Gortsema, J. Phys. Chem. Solids **24**, 863 (1963).
[13].   A. Jayaraman, V. Narayanmurti, E. Bucher and R. G Maines, Phys. Rev. Lett. **25**, 368 (1970).
[14].   Andreas Sousanis,Philippe,E.Smet and Dirk Poelman, Review Materials Mdpi ,**10,**953 (2017)
[15].   A. Jayaraman, V. Narayanmurti, E. Bucher and R. G Maines, Phys. Rev. Lett. **26**, 1430 (1970).
[16].   C. M. Verm and V. Heine, Phys. Rev. **11**, 4763 (1975).
[17].   L. L. Hirst, J. Phys. Chem. Solids **35**, 1285 (1974).
[18].   A. Jayaraman, A. K. Singh, A. Chatterjee and S. Usha Devi, Phys. Rev. **B9**, 2513 (1974).
[19].   P. W. Anderson and S. T. Chui, Phys. Rev. **B9**, 3229 (1974).
[20].   U. Benedict and W. B. Holzafel, Handbook on The Physics and Chemistry of Rare Earths (North Holland, Amsterdam, 1993), p. 113.
[21].   V.A.Sidorov,N.N.Stepanov,L.G.Khvostantsev,O.B.Tsiok,A.V.Golubkov,V.S.OskotsiandI.A.Smirnov,Semicond.Sci.Technol.**4**,286(1989)