Study of P-V Relationship and Transition Pressure in Samarium Chalcogenides

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The pressure volume relationships for samarium chalcogenides have been studied at high pressure (140 kbar -160kbar). An insulator to metal transition occurred due to an f^{n-1} atomic configuration and promoted an f-electron to a d-state. The density of state of a d-electron is small compared to the f-state. In this method, we numerically plotted the graph pressure versus fractional volume and obtained a trend similar to that of the experimental results. From the graph, we have determined the theoretical transition pressure and fractional volume during transition pressure. Using transition pressure and fractional volume, we calculated the deformation potential and $\frac{\partial E_g}{\partial P}$. The calculated values are compared with the experimental results.

1. Introduction

A notable property of samarium chalcogenides is that it is found to be in a semiconducting state when a samarium ion is divalent, and metallic when it is trivalent [1,2,3]. The pressure-volume studies in samarium chalcogenides [1,4,5] have shown that compounds undergo a pressure induced valence change from 2^+ towards 3^+ state due to the promotion of 4f electron. This method correlates the theoretical transition pressure, fractional volume at transition pressure, deformation potential, and $\frac{\partial E_g}{\partial P}$. Since the valence transformation involves the delocalization of the 4f electron and its merging with the conduction band at some high pressure, the occurrence and nonoccurrence of valence transformation in a certain range of pressure is determined by the magnitude of the 4f conduction band separation and the rate at which it decreases with pressure [6,7,8,9,10].

2. Theoretical Methodology

We have developed a model for determining the transition pressure, deformation potential, average frictional valence, and $\frac{\partial E_g}{\partial P}$ of samarium chalcogenides. From the numerical pressure-volume relationship data, we studied the theory of phase transition (Insulator to metal) in Samarium chalcogenides. We have analyzed the energy as a function of both the average number of s-d electron per atom Z and the average volume per atom V. The contribution to the energy is the sum of contributions of primarily electronic in nature and those that are primarily of lattice origin and is given by,

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

Since volume depends strongly on the valence of the samarium ion, this distribution is hardly precise. We emphasized the special features of the transition in the samarium chalcogenides, which may be said to arise from lattice effects. The process is limited by the fact that the density of state of d-electron is small as compared to that of the f-state, so that an increasingly larger energy is required to create a new $f^{n-1}d$ state. A microscopic derivation of this picture has been given by Heine and the author [11]. Related work on this problem has been done by Hirst [12] . We can write the lattice contribution of energy as:

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

Where, V_0 is the equilibrium volume.

We have included the variation of Bulk modulus on the volume [13],

$$B(V') = B(V)\left(\frac{V}{V'}\right)^{\gamma} \quad (3)$$

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with $\gamma = 1.3$.

The physics of a non linear term is that there will be the elastic interaction energy between ions of the same size. This interaction energy is always attractive if the lattice is purely harmonic, leading to a contraction of the lattice. The non-harmonic term can make a repulsive contribution to the interaction energy [14]. One-electron is contributed to $E_l(V,Z)$ of the promotion energy E_g from the f-level to the conduction band and the binding energy E_B. $E_l(V,Z)$ can be expressed in terms of promotion energy $E_g(V)$ and exchange energy and it is given by

$$E_l(V,Z) = Z\left[E_g(V)\theta(E_g) + E_B\right] + E_{xc} \quad (4)$$

Where, $\theta(E_g) = 1$, for $E_g(V) > 0$, (i.e., bottom of the conduction band above the f-level), and $\theta(E_g) = 0$, for $E_g(V) < 0$.

We assume that the decrease of E_g with decreasing volume [11] is given by

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

The coefficient β is adjusted by comparing the linear term with experimentally observed results. The variation of the d-electron bandwidth $W(V)$ is taken to be

$$W(V) = W(V')\left(\frac{V}{V'}\right)^{5/3} \quad (6)$$

The band energy E_B depends on volume and fractional valence [11] and the relation is given by

$$E_B = \frac{3}{5}\left(\frac{3}{\pi}\right)^{\frac{2}{3}} W(V) Z^{\frac{2}{3}} \quad (7)$$

The non-linear dependence may be taken to be of the same form as the bandwidth of the d-electrons. The total electronic energy must be calculated using the chemical potential for conduction electrons. The total energy is a function of average fractional valence Z, the volume V and the equilibrium condition

$$\frac{\partial E(Z,V)}{\partial V} = 0, \text{for } Z > 0 \quad (8)$$

This provides the relationship $Z(V)$ at equilibrium. For the equilibrium position to be stable, the determinate of the second derivatives of E with respect to Z and *V* must be positive. This condition can be easily shown to be equivalent to the condition that $\frac{dP}{dV} < 0$. One may write

$$-\frac{dP}{dV} = \frac{\partial^2 E}{\partial V^2} - \frac{\left(\frac{\partial^2 E}{\partial Z \partial V}\right)^2}{\frac{\partial^2 E}{\partial Z^2}} > 0 \quad (9)$$

for stability. Inserting $Z(V)$ obtained from (8) into (9) and integrating the equation of state, P versus V can be calculated. The calculations have been done numerically using MATLAB. The finite value of Z show the even transition in SmS. This is due to the $Z^{5/3}$ contribution of the binding energy. The phase transition in SmS 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 accommodate one electron per atom. The deformation potential can be calculated using the following formula [13],

$$\Sigma = \frac{E_g}{V/V_0 - 1} \quad (10)$$

Where, V/V_0 is the fraction of volume when the transition starts. Also we have

$$\frac{\partial E_g}{\partial P} = \frac{\Sigma}{B_0} \quad (11)$$

With the help of $\frac{\Sigma}{B_0}$, we can calculate $\frac{\partial E_g}{\partial P}$. In Fig. 1, we have plotted the graph pressure versus fractional volume and we determined the theoretical transition pressure of samarium chalcogenides. Using Table 1, we have calculated transition pressure, fractional volume, deformation

potential, and $\frac{\partial E_g}{\partial P}$. These calculated values are in close agreement with the experimental results and listed in Tables 2 and 3.

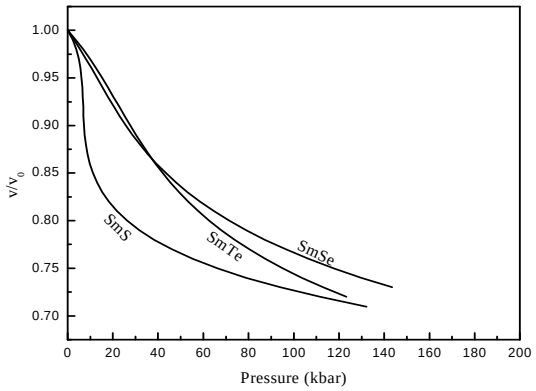

Fig.1: P–V relationship for the samarium monochalcogenides.

3. Conclusions

Pressure-volume studies helped understand and established the pressure-induced insulator to metal phase transition in samarium chalcogenides. We have calculated and studied the transition pressure and fractional volume at transition pressure (see Fig. 1). With the help of transition pressure and fractional volume, we can determine the deformation potential and $\frac{\partial E_g}{\partial P}$. The transition pressure, fractional volume at transition pressure, deformation potential and $\frac{\partial E_g}{\partial P}$ are calculated and listed in Tables 2 and 3. When we plotted the graph P versus $\frac{V}{V_0}$ (Fig. 1), we obtained the trend similar to that of the experimental result. The variation of fractional valence with pressure is shown in Fig. 2. The fractional valence increases at first linearly with an increase in pressure and increases slowly above the transition pressure. The transition pressure plays a major role in the theory of phase transition in samarium chalcogenides.

Table 1: Parameters used to calculate the equation of state in Figure 1.

Compd	B_0 (kbar)	γ	$E_g\left(P=0\right)$ eV	$W\left(P=0\right)$ eV
SmS	476	1.3	0.1	2.5
SmSe	520	1.3	0.5	2.5
SmTe	400	1.3	0.7	2.5

Ref. [11]

Table 2: Calculated transition pressure and volume changes of samarium monochalcogenides.

Compounds	Transition pressure (kbar)		Volume collapse (%)	
	Present	Others' works	Present work	Others' work
SmS	8.06	6.5[a], 12.4[b], 10[e]	13	13.5[a], 13.8[b], 11.1[e]
SmSe	20-60	40[a], 34[b], 30-90[c], 26-40[d], 33[e]	8	8[a], 11[c], 7[d], 9.8[e]
SmTe	20-57	20-80[a], 52[b], 60-80[c], 46-75[d], 62[e]	12	9[c], 7[d], 8.4[e]

[a]Ref. [15], [b]Ref. [16], [c]Ref. [17], [d]Ref. [18], [e]Ref. [19]

Table 3: Deformation potential and $\partial E_g / \partial P$ of samarium chalcogenides.

Compounds	Deformation potential (eV)		$\partial E_g / \partial P$ (meV/kbar)	
	Present	Others' work	Present	Others' work
SmS	–3.6	−4.7[a]	–7.5	−10[a]
SmSe	–6.25	−5.7[a]	–12	−11[b]
SmTe	–3.89	−4.7[a]	–9.72	−11[b], −11.9[c]

[a]Ref. [13], [b]Ref. [4,5], [c]Ref. [20]

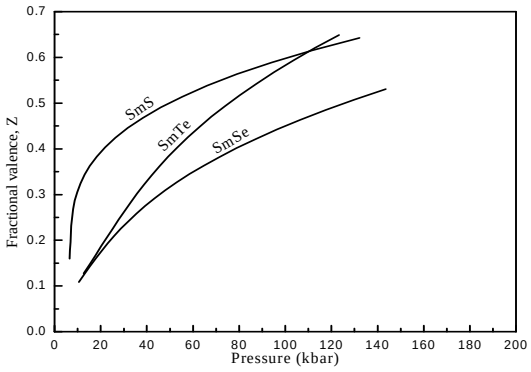

Fig.2: Fractional valence vs pressure for samarium monochalcogenides.

References

[1] A. Chatterjee, A. K. Singh and A. Jayaraman, Phys. Rev. **B6**, 2285 (1972).

[2] F. J. Reid, L. K. Matson, J. F. Miller and R. C. Himes, J. Phys. Chem. Solids **25**, 969 (1964).

[3] R. Didchenic and F. P. Gortsema, J. Phys. Chem. Solids **24**, 863 (1963).

[4] A. Jayaraman, V. Narayanmurti, E. Bucher and R. G Maines, Phys. Rev. Lett. **25**, 368 (1970).

[5] A. Jayaraman, V. Narayanmurti, E. Bucher and R. G Maines, Phys. Rev. Lett. **26**, 1430 (1970).

[6] W. A. Basset, T. Takahashi and W. P. Stook, Rev. Sci. Instr **38**, 37 (1967).

[7] D. B. Mcwhen and W. L. Bond, Rev. Sci. Instr. **35**, 626 (1964).

[8] A. K.Singh, Rev. Sci. Instr. **43**, 134 (1972).

[9] D. L. Decker, J. Appl. Phys. **36**, 157 (1965).

[10] L. Liu and W. A. Basset, J. Appl. Phys. **44**, 1475 (1973).

[11] C. M. Verm and V. Heine, Phys. Rev. **11**, 4763 (1975).

[12] L. L. Hirst, J. Phys. Chem. Solids **35**, 1285 (1974).

[13] A. Jayaraman, A. K. Singh, A. Chatterjee and S. Usha Devi, Phys. Rev. **B9**, 2513 (1974).

[14] P. W. Anderson and S. T. Chui, Phys. Rev. **B9**, 3229 (1974).

[15] U. Benedict and W. B. Holzafel, *Handbook on The Physics and Chemistry of Rare Earths* (North Holland, Amsterdam, 1993), p. 113.

[16] V. A. Sidorov, N. N. Stepanov, L. G. Khvostantsev, O. B. Tsiok, A. V. Golubkov, V. S. Oskotsi and I. A. Smirnov, Semicond. Sci. Technol. **4**, 286 (1989).

[17] T. Le Bihan, S. Darracq, S. Heathman, U. Benedict, K. Mattenberger and O. Vogt, J. Alloys. Comp. **226**, 143 (1995).

[18] O. B. Tsiok, V. A. Sidorov, V. V. Bredikhin, L. G. Khvostantsev, A. V. Golubkov and I. A. Smirnov, Solid State Commun. **79**, 227 (1991).

[19] W. M. Temmarman, A. Svane, L. Petit, M. Luders, P. Strange and Z. Szotek, Phase Transition **80**, 415 (2007).

[20] C. M. Verma, Rev. Mod. Phys. **48**, 219 (1976).

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