THEORY OF PHASE TRANSITION IN RARE EARTH CHALCOGENIDE COMPOUNDS

Adhikari, D.R., Subedi D.P., Singh,V.K.*

Department of Natural Sciences,
Kathmandu University, Dhulikhel, Kavre, P.O. Box: 6250, Kathmandu, Nepal.
*Department of Physics, D.S. Post Graduate College, Aligarh (India).

ABSTRACT
In a number of rare earth chalcogenide compounds [(SmX, YbX, EuX)] where X=S, Se and Te], the atomic-like f levels and the wide s-d band co-exist at the Fermi level. Such compounds are considered mixed -valence compounds and ionic semiconductor at atmospheric pressure.

INTRODUCTION
The atoms of all rare earth elements except Eu,Sm and Yb exist in trivalent state. The divalent Eu Sm and Yb are particularly ideal as most of them are semiconducting (Galubkov 1966 and 1963, Jayaraman 1970) and ionic. Rare earth chalcogenides are found in a semiconducting state when the rare earth ion is divalent and in a metallic state when the some rare earth ion is trivalent. This being its notable, we can consider an expression for the thermal expansion coefficient. Here the dependence of volume on pressure as a result of the direct dependence due to anharmonicity and also a result of the variation of z with pressure. Therefore,

$$K = \frac{1}{V}\frac{dV}{dP} = \frac{1}{V}\frac{\partial V}{\partial P} + \frac{1}{V}\frac{\partial V}{\partial z}\frac{\partial z}{\partial P} \quad \ldots\ldots\ldots\ldots \quad (1)$$

However, z depends on the volume, since the volume determines the gap E_g in the insulating phase the Fermi energy E_f (which is pinned to the f level) in the metallic phase. Thus we will have,

$$\frac{\partial z}{\partial P} = g(p)\frac{dV}{dP} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Suppose, we are in insulating phase with gap $E_g(V,P)$then,

$$Z(p) = \int_{E_g(V,P)}^{w} d\varepsilon \rho(\varepsilon) f(\varepsilon, P) \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where $\rho(\varepsilon)$ is the density of states in the conduction band, $f(\varepsilon,P)$ is the Fermi function and W is the band width of the conduction band. For pressures that we are concerned with, we will take W to be ∞. Ignoring for the moment the higher lying f level. We get,

$$Z(P) \approx e^{-Eg/P} y(x) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$Z(P) \approx e^{-Eg/P} y(E_g/P) \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Where y(x),x=(E_g /P) depends up on the band structure and is slowly varying on the scale of exponential. Then taking in to account the fact, the E_g also depends on pressure and using,

$$\frac{dE_g}{dP} = \frac{\partial E_g}{\partial V}\frac{\partial V}{\partial P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Now,

$$K(P)= \frac{K_0}{1-\alpha\beta y(E_g / P)e^{E_g / P}} \qquad (7)$$

Where,

$$\alpha=-\frac{1}{V}\frac{dV}{dz}>0 \qquad (8)$$

and

$$\beta=V\frac{dE_g}{dV}>0 \qquad (9)$$

Here

Equation (12) must be solved together with

$$E_g(P)= E_g(0)+\beta\int_0^P K(P')dP' \qquad (10)$$

Generally as (E_g/P) increases, y (E_g/P) increases, at $E_g=0^-$, we have an stability for $P=0^+$ because K(P) is negative. Which makes $E_g(P)$ less than zero. As we increase E_g slightly, if the denominator is negative, we will have thermal contraction, which tends to decrease E_g still further, leading to further contraction. The factor f (E_g/P) etc. tends to slow down the contraction. By a balance of these factors, we can have the denominator going to zero, in finite contraction and a transition to the metallic state. If E_g is large enough. We will start at low pressure with the thermal expansion removes any instability. Had we concluded the higher lying f states, the qualitative picture would remain the same, but the instability would occur generally at higher pressures. By inserting numbers in equation (7) the above scenario can be seen reasonable. If there will be a metallic transition as P is increased, and the larger the $E_g(0)$,the larger P transition. If there is a thermal expansion, the bottom of the d level moves up relative to the f level (Chatterjee 1972).This further increases the volume and so on, till at high enough pressure.$E_g(P)\rightarrow 0$,and we have regained a semiconductor,

Now,

$$N_d= \int_{-E_c(p)}^{0} \rho(\varepsilon)f(\varepsilon, p)d\varepsilon \qquad (11)$$

Where $-E_c(P)$ is the bottom of the conduction band relative to the f level (and Fermi level) at 0,and calculate g(P) and K(P) together with,

$$E_c(P)=E_c(0)=dE_c/dV +\int_0^P K(P')dP' \qquad (12)$$

Combining equation (6) and (7)

$$K= \frac{K_0}{[1- g(P)\partial V / \partial z]} \qquad (13)$$

Where K_0 is the lattice thermal expansion coefficient and when change of z with pressure is negligible. In this method, we can apply only to semiconductors and metals because of the dependence of activation energy on the energy gap varying with pressure. This way metallic behaviour has been shown at high pressure.

CONCLUSION

Phase transition in rare earth chalcogenides and the energy gap between conduction band and valence band depends on the pressure. At atmospheric pressure, they are in semiconducting

level when we increase in pressure. Semiconducting behaviour goes towards the metallic behaviour and eventually overlaps at high-pressure. The pinning of the fermi level due to the f levels is the hybridization of the f and s-d states, strongly coupling for the interactions of the f and s-d electrons and consequently strong excitonic correlations. This method gives the thermal conductivity, the impurity carrier concentration and conduction band gap, which are function of pressure.

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