The critical point for the isostructural black to metallic phase transition in SmS has been determined using thermoelectric power as a probe. The magnitude of the thermo-power anomaly accompanying this electronic phase transition continuously decreases with the increase of temperature. Further the pressure hysteresis between the forward and reverse transitions progressively decreases as the critical point is approached. The present study indicates that the critical point is close to 825°C.

The iso-structural electronic phase transformation in rare-earth systems like Ce, SmS and other similar compounds has been the subject of numerous experimental and theoretical investigations in recent years. It is of interest that in some of these systems like Ce, the γ-α phase boundary terminates at a critical point. The pressure-induced first-order electronic transition in SmS was studied up to 250°C by Jayaraman et al. using resistivity and DTA as tools. They observed that the semiconductor-metal (S-M) phase boundary is steep (~300°C/kbar) and has a positive slope. Recently Tomkov and Aptekar have investigated the phase stability diagram of SmS from -60°C to +500°C using DTA. These authors predict a critical temperature of 700°C for the S-M phase boundary based on their observed decrease in the pressure hysteresis with rising temperature.

In this note we present data on the thermo-electric behaviour of SmS up to 835°C which gives direct experimental evidence for the existence of a critical point in SmS. We reported earlier the thermoelectric behaviour of SmS at 30°C as a function of pressure. The semiconductor to metal transition occurring near 6.5 kbar pressure at 30°C manifests itself as a large discontinuity (~70 μV/°C) in the thermo-power (Q) versus pressure (P) graph. The present study indicates that the magnitude of the thermo-power anomaly and the pressure hysteresis vanish around 825°C, the critical temperature for the S-M phase boundary. A phase diagram constructed out of our experimental results is also presented.

Figure 1 gives different isotherms of Q versus P for the S-M transition in SmS. The experimental techniques used for collecting these data have been described earlier. The data below 300°C were obtained using the teflon cell technique with silicone fluid as the pressure transmitting medium. For temperatures greater than 300°C, hexagonal boron nitride which is a good pressure transmitter especially at high temperatures was used. Great care has been taken to minimize the inhomogeneous pressure distribution over the sample by using very small samples (~0.5mm x 0.5mm x 0.2mm). The sharp discontinuity in the Q versus P isotherm at 530°C gives direct evidence of the uniform pressure distribution over these samples.

The experiments were performed with line pressure (which is the pressure of the hydraulic fluid before the intensifier) measurements accurate to ±0.50 bars. Temperatures were maintained constant by slow pressure variation and the accuracy in temperature
measurement was ± 5°C. It is clear from Fig. 1 that the magnitude of the thermopower anomaly at the phase transition decreases with increase of temperature. This behaviour is very similar to the one observed with the y-a transition in cerium. The isotherm at 715°C definitely shows the existence of the anomaly near the transition, thereby indicating that the critical point is above 700°C. The isotherm at 835°C is continuous through the phase transition which gives direct evidence for the S-M phase boundary terminating at a critical point.

The continuous line in Fig. 2 gives the phase diagram of SmS constructed out of the present thermopower data. The difference in the pressures at which the forward and reverse transitions occur which is of the order of 5 kbar at 25°C progressively narrows down at higher temperatures. The circles on the dashed line in Fig. 2 correspond to the pressure at which the metallic phase comes back to the black phase on releasing the pressure at that particular temperature. The temperature at which the hysteresis interval closes down is around 825°C. This is consistent with the continuous variation of Q with pressure at 835°C (inset in Fig. 1). Our data up to 835°C gives for dT/dP a value of 170°C/kbar which is considerably lower than the ones reported earlier.

On the theoretical side the phase diagram for SmS has been worked out by Wio et al. (1974) who used a simple ionic model for the cohesive energy and electronic terms similar to those of the Falicov-Kimball model for metal-insulator transitions. This theory predicts a critical temperature of 280°C and, moreover the slope of the T-P plot turns out to be negative. It is worth pointing out that these authors have not considered the lattice contribution to the entropy which would be important at higher temperatures. There has been another formulation of the equation of state for mixed valence compounds due to Groncalves da Silva and Falicov (1975) which is a modification of the original Falicov-Kimball model and includes the effects of hybridization between the localized and itinerant states. This theory again leads to a negative slope in the T-P diagram. However, these authors point out that this disagreement with the earlier results of Jayaraman et al. (1975) is due to the neglect of the entropy associated with the localized magnetic moments which would stabilize the semiconducting phase at higher temperatures. On the basis of the Clausius-Clapeyron relation, a positive slope in the T-P plot implies that the entropy of the mixed valence phase is lower than that of the semiconducting phase in the temperature region of measurement. The significance of the present experimental determination of the critical point for the S-M transition in SmS is that the critical temperature is around 825°C which is much higher than the theoretical estimate of Wio et al. (1974) and further it confirms the positive slope of dT/dP.

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