Resistivity and thermo-electric behaviour of some mixed-valence systems at high pressures and high temperatures

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Resistivity and thermo-electric behaviour of some mixed-valence systems at high pressures and high temperatures

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Résumé. — Dans cet article nous présentons quelques résultats nouveaux sur les propriétés de transport de SmS et $Sm_{0,8}Tb_{0,2}S$ aux fortes pressions. Utilisant le pouvoir thermo-électrique, nous avons trouvé que la ligne de changement de phase pour la transition métal-semiconducteur se termine à un point critique pour SmS. En outre, le comportement de $Sm_{0,8}Tb_{0,2}S$ aux fortes pressions indique que les ions Sm sont dans l'état complètement trivalent en dessus de 12 kbar.

Abstract. — This paper reports some new data on the transport properties of SmS and $Sm_{0.8}Tb_{0.2}S$ at high pressures. Using thermo-power as a tool, we have established that the semiconductor-metal phase boundary in SmS terminates at a critical point. Further the high pressure behaviour of $Sm_{0.8}Tb_{0.2}S$ suggests that at pressures greater than 12 kbar, the Samarium ion is in the fully trivalent state.

1. **Introduction.** — The electronic transformation in rare-earth systems has received considerable attention in recent years [1]. The semiconductor-metal transition in SmS in the *P-T* plane has been studied by Jayaraman *et al.* [2] up to 250 °C and by Tonkov and Aptekar [3] up to 500 °C. The present study involving thermo-power and resistivity as tools is aimed at establishing the critical point for S-M phase boundary. Further the high pressure behaviour of thermo-power and resistivity in *chemically collapsed* $Sm_{0.8}Tb_{0.2}S$ suggests that at high pressures the Samarium ion is in the fully trivalent state.

2. **Results.** — The experimental techniques for thermo-power and resistivity measurement at high pressures have been described elsewhere [4]. Figure 1 gives the different isotherms of thermopower (Q) *versus* pressure (P) for SmS. It is clear that the magnitude of the thermo-power anomaly at the first-order phase transition decreases with increase of temperature. The inset in figure 1 corresponding to 835 °C shows that the first-order phase transformation in SmS has become continuous around this temperature. We have also used the progressive narrowing of the pressure hysterisis with increasing temperature as a criterion to track the critical point. Figure 2 shows the phase diagram of SmS constructed out of the present thermo-power data. The solid line corresponds to the phase transformation pressures for the forward transition and the dotted line to the reverse transformation. The hysterisis interval closes around 825 °C which is consistent with the continuous variation of Q with P at 835 °C (inset in figure 1). The present data gives clear evidence for the S-M phase boundary terminating at a critical point which is around 825 °C. Further the slope of the *T-P* plot is positive and has a value of 170 °C/kbar.

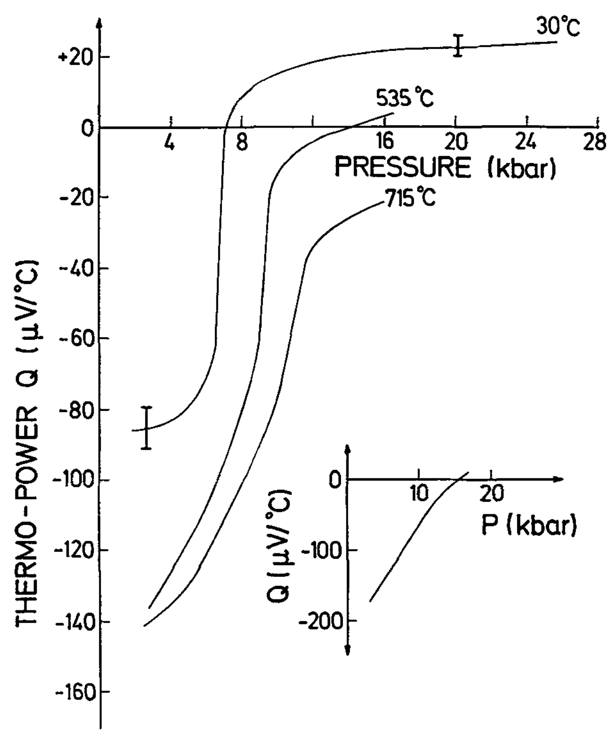

Fig. 1. — Isotherms of thermo-power *versus* pressure for SmS.

The resistivity behaviour with pressure of $Sm_{0.8}Tb_{0.2}S$ is shown in figure 3. It is seen that over a narrow pressure interval of 5 kilobar, resistivity decreases rapidly with pressure although at higher

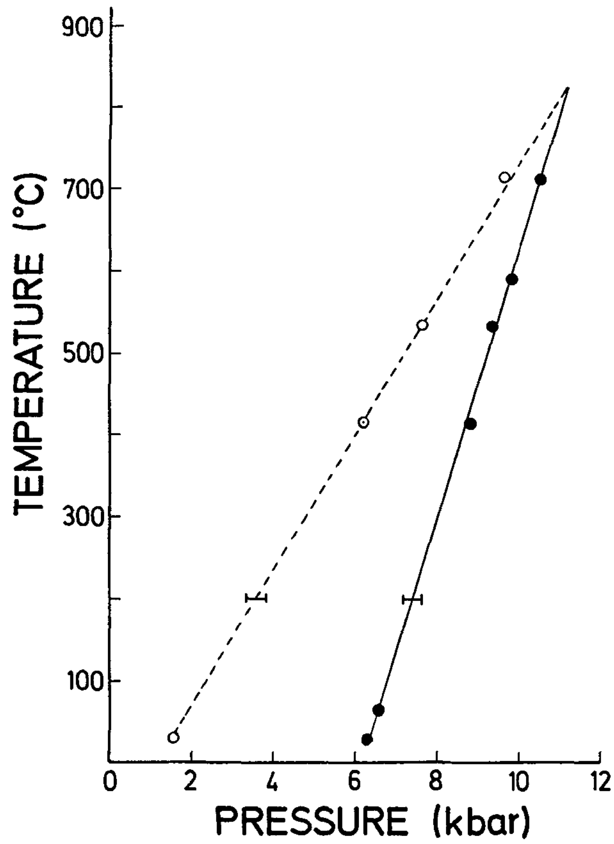

Fig. 2. — Phase diagram of SmS from the present data.

temperatures this decrease becomes less rapid. Our previous data [5] shows that thermo-power anomalously increases in the same pressure interval. The temperature behaviour of resistivity is shown in figure 4. At low pressures the behaviour is similar to that of a semi-metallic substance. However at higher pressures, resistance increases linearly with temperature, typical of a trivalent rare-earth chalcogenide. These results indicate that at higher pressures, Samarium ion is in the fully trivalent state.

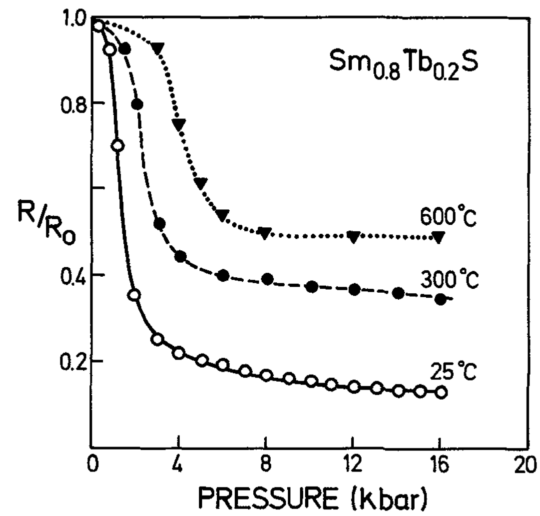

Fig. 3. — Relative resistance *versus* pressure for $Sm_{0.8}Tb_{0.2}S$.

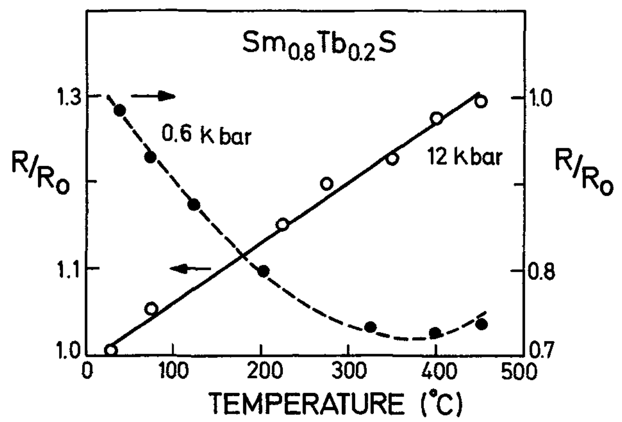

Fig. 4. — Isobars of relative resistance *versus* temperature for $Sm_{0.8}Tb_{0.2}S$.

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