PRESSURE-INDUCED ELECTRONIC TRANSITIONS IN RARE-EARTHS

S. Ramaseshan, T.G. Ramesh and V. Shubha
Materials Science Division
National Aeronautical Laboratory
Bangalore, India

INTRODUCTION

The discovery of pressure-induced electronic phase transitions in rare-earth chalcogenides like SmS (1,2) has led to a spurt of experimental and theoretical activity in recent years (3-5). The phenomenon of valence instability associated with the 4f shell in these rare-earth compounds has attracted particular attention, considering the fact that most of the rare-earth ions in metals, alloys and intermetallic compounds are integral valent and remarkably indifferent to their physical and chemical surroundings. Among the rare-earth metals, cerium is unique in that it undergoes a pressure (or temperature) induced valence transition and its α-phase has intermediate valency much like that in the high pressure phase of SmS (6). It is also observed that pressure can remove the overlap between two energy bands causing a continuous electronic transition. The metal-semiconductor transition in ytterbium (Yb), a divalent rare earth metal, near 13 kbar pressure is a typical example.

In this paper we review the electronic properties of the valence fluctuating systems viz., Ce, SmS and chemically collapsed compounds like $Sm_{0.84}Gd_{0.16}S$. The emphasis will be on the behaviour of the thermo-electric power (TEP) in the mixed-valent phase of these systems (7,8). The experimental phase diagram of SmS in the P-T plane (8) and the theoretical predictions of several models are considered in some detail. Studies on cerium include the anomalous pressure variation of TEP in the γ-phase (9) and the recent observation of Kondo-like anomaly in γ-Ce (10). These provide new supporting evidence that a 4f virtual bound state (VBS) resides in close proximity with the Fermi level. Some new results on the pressure induced metal-semiconductor transition in ytterbium are also presented (11,12).

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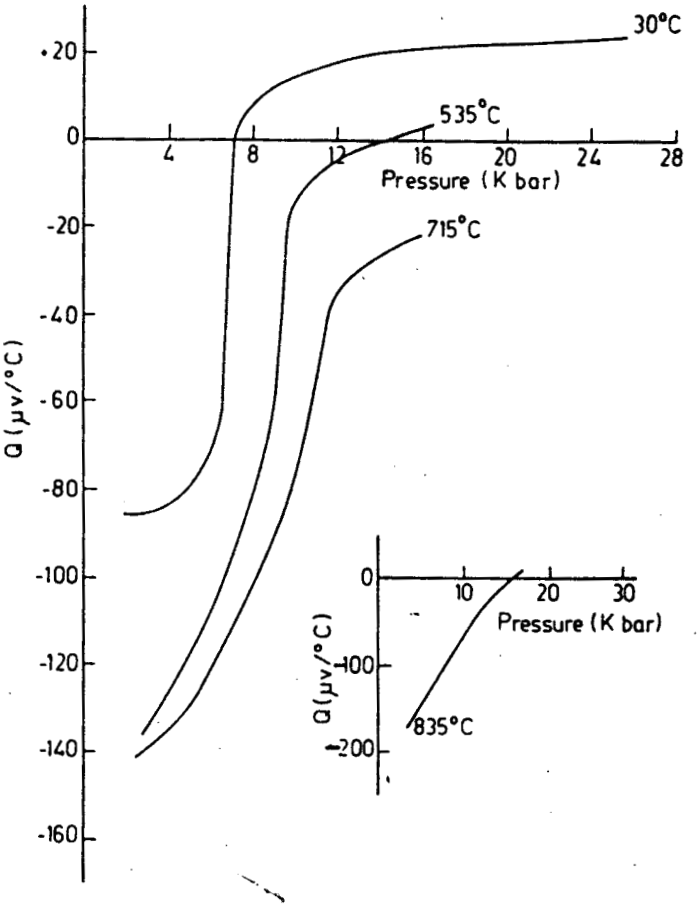

Fig. 1. Isotherms of TEP versus pressure for SmS.

VALENCE FLUCTUATION IN SmS

SmS crystallizes in the NaCl type structure having lattice parameter 5.97 Å and undergoes a strongly first order isostructural phase transition at 6.5 kbar at room temperature. This is a spectacular phase transition in the sense that the black semiconducting phase (S-phase) turns golden yellow (M-phase). This electronic transition has been studied using several diagnostic tools like resistivity, volume compression, Mössbauer effect, photoelectron spectroscopy, etc. (13,5). It will suffice here to note that the high pressure phase of SmS is a intermediate valence system with a rapid fluctuation between

two degenerate configurations viz, $4f^6 5d^0$ and $4f^5 5d^1$, which are pinned at the Fermi energy (14). The electronic specific heat in the collapsed phase is anomalously large 145 mJ/^{o}mole-^{o}K^2 indicating the presence of a high density of states at E_F.

TEP BEHAVIOUR OF SmS

Polycrystalline samples of SmS prepared by the procedure given by Bucher (1) were used in the present studies. The experimental techniques for TEP measurement at high pressures and high temperatures have been described earlier (15). Figure 1 gives the isotherms of TEP vs pressure for SmS (8). In the S-phase TEP is large and negative $\simeq -80\mu V/^oC$ at 30^{o}C. The first order phase transition near 6.5 kbar associated with the 4f-5d electron delocalization manifests itself as a sudden drop in the magnitude of TEP together with a change of sign. In the region prior to the phase transition TEP decreases considerably with pressure. The notable feature of this diagram is that the magnitude of the discontinuity in TEP at the phase transition decreases progressively with temperature. The isotherm corresponding to 835^{o}C is almost continuous with pressure suggesting that this S-M phase boundary terminates in a critical point. The progressive narrowing of the pressure hysteresis between the forward and the reverse transition with increase in temperature is also used as a criterion to track the critical point. Figure 2 depicts the phase diagram of SmS constructed out of the present experimental data. The solid line gives the transformation pressures corresponding to the forward transition while the dotted line corresponds to the reverse transition. It is clear that the difference in pressure at which the forward and reverse transition occur ($\sim$5 kbar at 25^{o}C) progressively narrows down at higher temperatures. The temperature at which the magnitude of the TEP anomaly vanishes and the hysteresis interval closes down is around 825^{o}C. This is consistent with the continuous variation of Q with P at 835^{o}C (inset of Figure 1). We believe that the critical temperature for S-M phase boundary is around 825^{o}C (8). Our data shows that dT/dP is positive and has a value of 170^{o}C/kbar which is considerably lower than the earlier estimates (13). It is worth pointing out that the phase diagram of SmS has close similarities with the γ-α phase boundary in Ce. The implications of the phase diagram viz., the critical point and the positive slope of the T-P plot in relation to the mixed valence problem will be discussed later.

The variation of TEP with pressure in the high pressure phase of SmS (Figure 3) is quite anomalous in that over a narrow

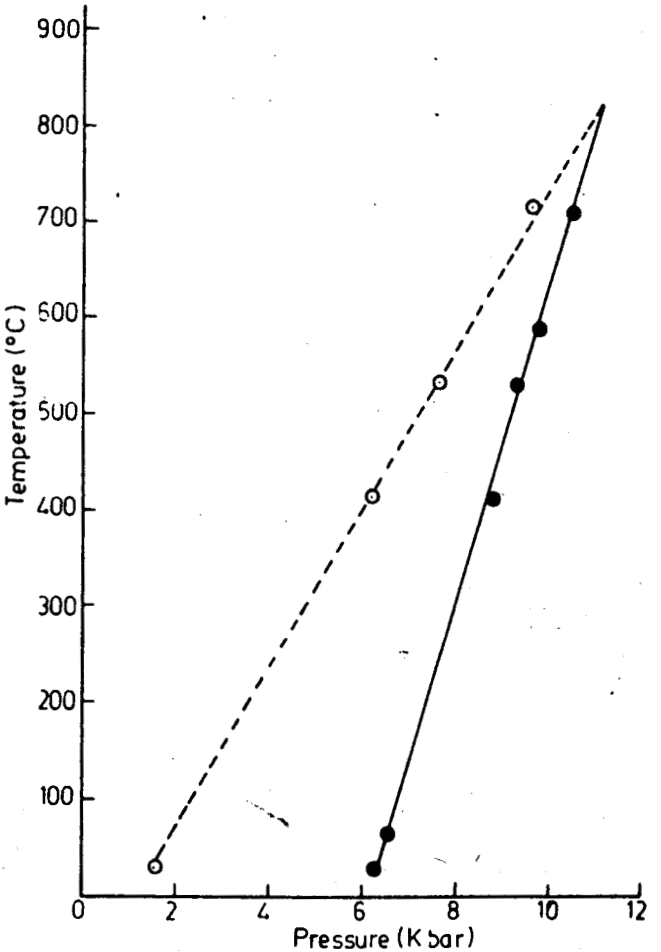

Fig. 2. Phase stability diagram in SmS.

pressure range between 8 and15 kbar TEP increases steeply from ∿0 to +10 μV/°C. Also shown in Figure 3 is the TEP behaviour of critically doped and chemically collapsed SmS viz., $Sm_{0.84}Gd_{0.16}S$, which is remarkably identical to that in the high pressure phase of SmS indicating the close similarity in their electronic structure.

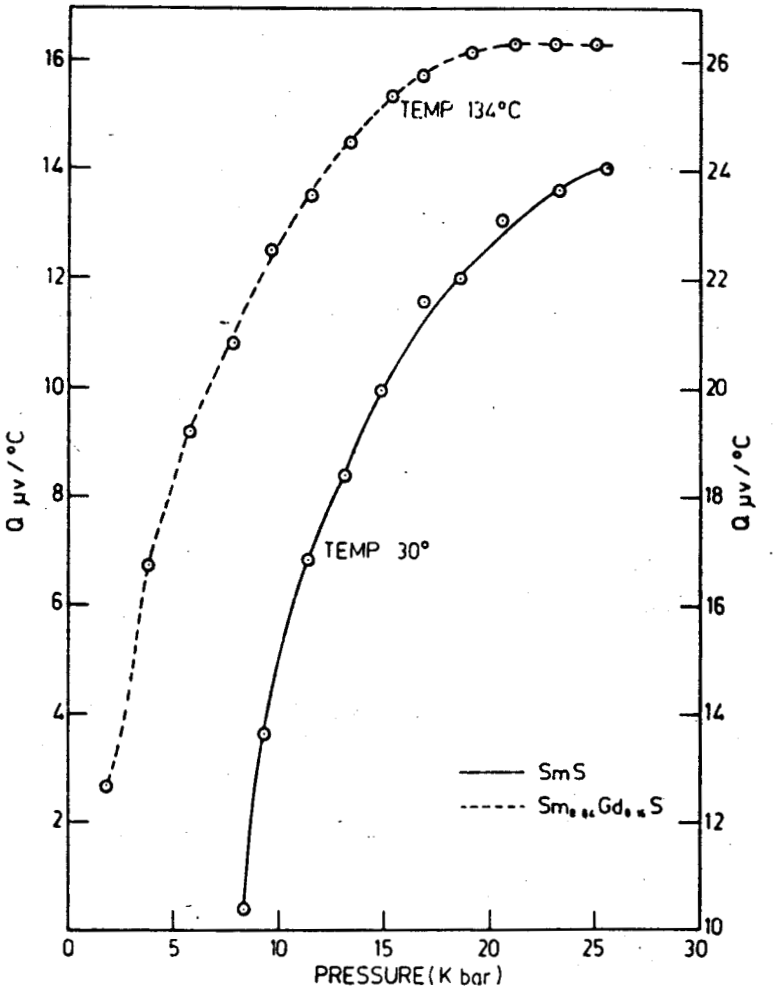

Fig. 3. Anomalous pressure dependence of the TEP in $Sm_{0.84}Gd_{0.16}S$ and in the high pressure phase of SmS. (Scale of Q for SmS on L.H.S.)

PHASE DIAGRAM OF SmS

The unique features of the phase diagram of SmS are (a) the existence of a critical point around 825°C and 11 kbar and (b) the large positive slope in the T-P diagram. We present a critique of the various theoretical models developed to

explain the phase diagram of SmS and focus attention on some of the theoretical problems yet to be understood.

Application of the Clausius-Clapeyron relation viz., $dT/dP = \Delta V/\Delta S$ to the S-M phase boundary shows that ΔS is negative for dT/dP to be positive, as ΔV is always negative in a pressure experiment. This means that the entropy of the semiconducting phase is higher than that in the metallic phase. The ground state of the Sm^{2+} ion appropriate to the S-phase has J=0 and hence no spin disorder entropy whereas the pure configuration Sm^{3+} ion has J = 5/2. Thus if the valence transition had proceeded all the way to the pure trivalent configuration state, then it would lead to a negative slope in the T-P diagram. The situation in SmS is quite different from that in Ce because Ce^{3+} ion in γ-phase has J = 5/2 giving rise to a finite spin disorder entropy. It is conceivable that a strong reduction of this spin disorder entropy accompanying the γ-α transition could give rise to a positive slope in the phase diagram.

On the theoretical side, the phase diagram for SmS has been worked out by Wio et al (16) 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. In setting up the free energy function, they neglected the entropy contributions from the conduction band and the lattice and took into account only the contribution from the holes in the 4f shell. This theory predicts a critical temperatures of only 280°C and moreover the slope of the T-P plot turns out to be negative. Goncalves da Silva and Falicov (17) have provided another formulation of the equation of state taking into account the hybridization between the localized and itinerant states. This theory again predicts the wrong slope. It is clear that in all these formulations, the entropy of the mixed valence phase turns out to be higher than that in the semiconducting phase.

Kaplan and Mahanti (18) proposed a two level model involving an f^2 spin singlet and fd spin singlet (instead of f^6 and f^5d) at each Sm site. In the mean field approximation they worked out the consequences of this model in relation to the phase diagram. They predict that the first order phase boundary terminates in a critical point around 1500°K. Although the order of magnitude estimate of T_c is close to the experimental value, the shape of the first order boundary had the wrong slope. This was attributed to the limitations of the two level model and in a later work (19) they have carefully considered all the entropy contributions in the semiconducting and metallic phases. In the S-phase the ground state of Sm^{2+} is $^7F_0$ (J=0) with $^7F_1$ (J=1) level lying about 400°K above and the next critical state $^7F_2$ lies about 1000°K from the ground

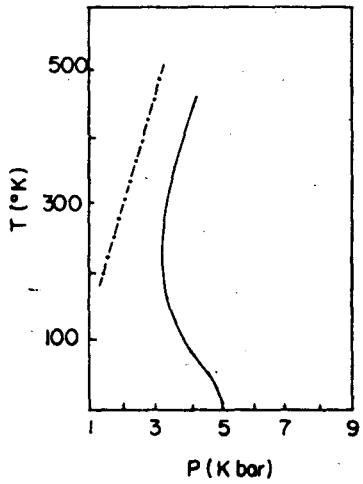

Fig. 4. Theoretical phase diagram of SmS (Ref. 19).

state. In the temperature regime of interest (>100°K), the J=1 level will be substantially occupied and this intra-site entropy has to be considered. The calculation of the entropy in the M-phase is complicated and is the crux of the problem. The distinctive feature of this model compared to all the other models is that at the phase transition only a small fraction ∿0.1 electron/atom goes over into the broad conduction band, the remaining still localized around the Sm ion. The electronic entropy then turns out to be

$$S_\alpha/k_B = \alpha \ln 6 - \alpha \ln \alpha - (1-\alpha) \ln (1-\alpha) \qquad (1)$$

where α is the number of electrons or holes per ion at this temperature. The lattice or phonon contribution is quite important and need to be taken into account. The experimental observation of soft bulk modulus accompanying the S-M transition in SmS implies that this would increase the entropy of the M-phase. The theoretical phase diagram according to this model is shown in Figure 4. The physical reason for obtaining a positive slope is due to the strongly reduced electronic entropy term in this essentially localised model. The electronic transition ($4f^6$-$4f^5 5d^1$) results in electric dipoles ordered in some complicated antiferroelectric arrangement which would not contribute to the entropy. As yet there is no ex-

perimental confirmation of this aspect of the model. This is in marked contrst to the other conventional models where a substantial fraction ~0.7 electron/ion gets delocalized. In the band model for T >100°K, the electron entropy in the metal will be approximately 0.7 $k_B$ln6 + 0.3 $k_B$ln4. Here ln6 is the entropy contribution of the J = 5/2 ground state of the Sm^{3+} ion. This is clearly greater than $k_B$ln4 which is the approximate electron entropy in the semiconducting phase. This alone gives $\Delta S > 0$. The lattice contribution will further increase ΔS. Thus it is difficult to see a significant negative contribution to the entropy of the M-phase in any band model.

The change of slope from positive to negative value for temperatures less than 100°K which at the present moment is a theoretical conjecture (4,19) is a general consequence of the fact that the entropy of the metal is approximately γT (electronic specific heat). This is much larger than the entropy in the S-phase as $T \to 0$. The turn around in the phase diagram around 150°K implies that this electronic entropy is exhausted around this temperature. The 4f electrons which appear to be in a coherent hybridized band at low temperatures seems to go over into the VBS regime at high temperatures. The low temperature resistivity (5) shows that the S-M transformation shifts to higher pressures which can be taken as an indirect evidence for the negative slope at low temperatures.

In summary, we note that the different aspect of the phase diagram of SmS present a challenge to the theoretical models. The conventional or the band type of models cannot really account for the higher entropy of the semiconducting phase. The localized model although capable of explaining this feature poses some difficulties in understanding other experimental data. Another problem of considerable experimental and theoretical interest is while SmS shows a discontinuous transition at room temperature, the closely related compounds SmSe and SmTe show a continuous phase transformation. The present studies clearly establish that even in SmS the phase transition is continuous above the critical point. A plausible explanation for the continuous transitions in SmSe and SmTe is that they have a much lower critical temperature. Experiments at low temperature and high pressures are required to confirm this point.

DISCUSSION OF TEP RESULTS

The anomalous variation of TEP in the high pressure phase of SmS and in the doped system $Sm_{0.84}Gd_{0.16}S$ finds a simple explanation. According to the Hirst model the valence fluc-

tuations on different rare earth sites are uncorrelated which is a good approximation at high temperatures. Then the rare earth ions which are in $4f^5 5d^1$ configuration act as resonant scatterers for the delocalized 5d electrons. Making the plausible assumption that the energy dependence of the relaxation time makes the main contribution (7), the expression for TEP under these conditions takes the form

$$Q_{res} = \frac{2\pi^2 k_B^2 T}{3|e|} \quad \frac{E_{4f} - E_F}{(E_{4f}-E_F)^2+\Delta^2/4} \qquad (2)$$

where Δ is the width of the 4f VBS and E_F is the Fermi energy. When E_F is pinned to E_{4f} which is the prerequisite for a valence fluctuating system, Q will be very small. Thus although the resonance scattering makes a large contribution to resistivity, its contribution to TEP is small. This accounts for the small magnitude of TEP at the phase transition. The anomalous increase in the magnitude of TEP with pressure can be understood if one assumes a downward displacement of the Fermi level with respect to the centre of 4f resonance. The experimental observation as derived from the lattice parameter data suggests that there is an increase in the fractional valence with pressure. This is equivalent to the Fermi level scanning the lower half of the 4f resonance. These small shifts within the width of 4f VBS is quite essential to account for the variation of fractional valence with pressure. The positive sign and the dramatic increase of TEP with pressure is due to the increase of $E_{4f}-E_F$ with pressure and is obvious from the expression for Q.

γ-α TRANSITION IN Ce

The pressure induced γ-α electronic transition in Ce and the anomalous properties of the mixed valent α-phase has been reviewed in several articles (5,6). Here we discuss briefly the TEP behaviour in the γ-phase which throws light on the position of 4f VBS relative to the Fermi energy. Figure 5 gives the TEP vs pressure plot at room temperature (9). It is remarkable that in the γ-phase TEP increases markedly with pressure and shows a cusp like anomaly and its variation with pressure has been satisfactorily accounted for on the basis of 4f VBS residing close to E_F (within 0.1 eV) in γ-Ce. In a recent study it has been established that γ-Ce is a Kondo-compound very similar to $CeAl_2$. There is a large pressure enhancement of Kondo-like anomalies both in TEP and resistivity. These new

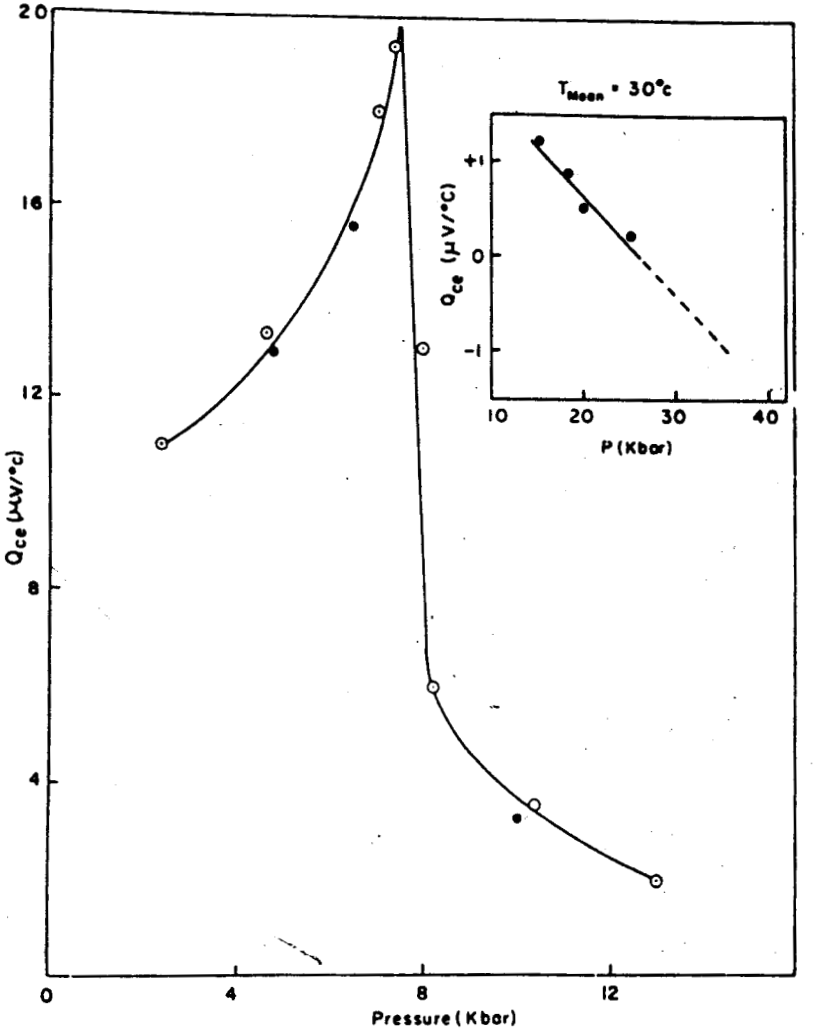

Fig. 5. Thermo-electric power versus pressure graph for Cerium at 30°C.
o - Data points obtained using Mo-W thermocouple.
O - Data points obtained using Chromel Alumel thermocouple.

observations suggest that the coupling of the conduction electrons with the 4f local moment is antiferromagnetic in nature. All these experimental findings support the promotion model where in the 4f VBS lies close to E_F. There is another conjec-

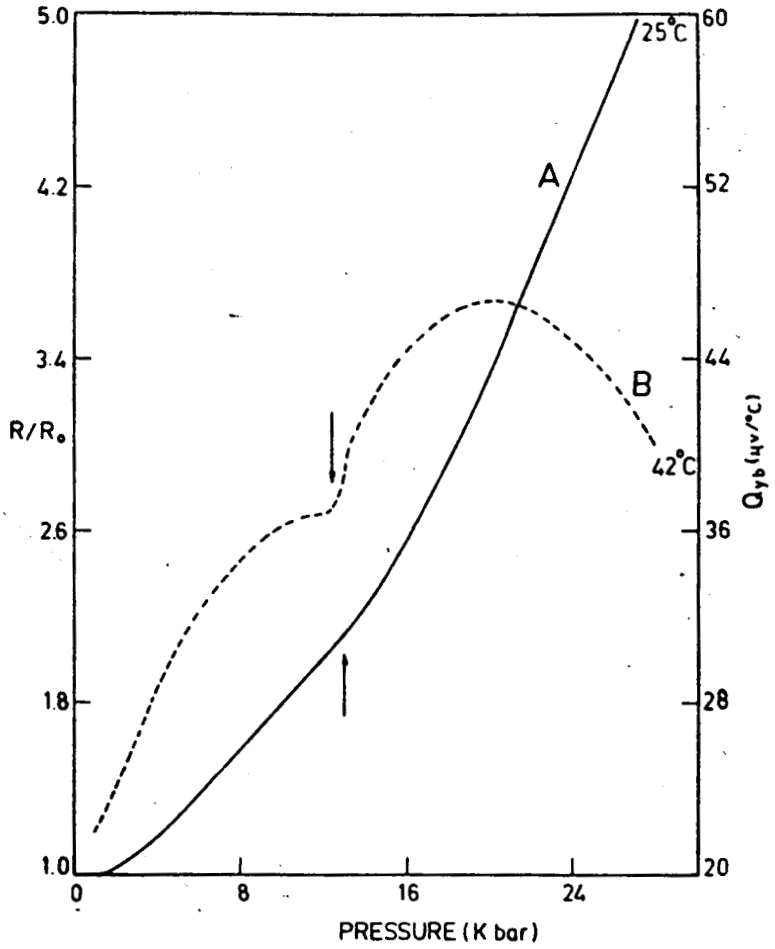

Fig. 6. R/R_0 (curve A) and TEP (curve B) against pressure. Position of arrows indicate the semimetal-semiconductor transition.

ture that the γ-α transition is a Mott transition (20) which does not require the presence of a closely lying 4f VBS. The x-ray photoemission studies on γ-Ce suggest that the 4f state is about 1.8 eV (5) below E_F and this is generally considered to favour the above viewpoint. However, the XPS does not probe the ground state of the system, unlike the measurements like resistivity and TEP. Optical absorption experiments on oxidised Ce sample which would locate the 4f state directly would greatly help in clearing up this controversy.

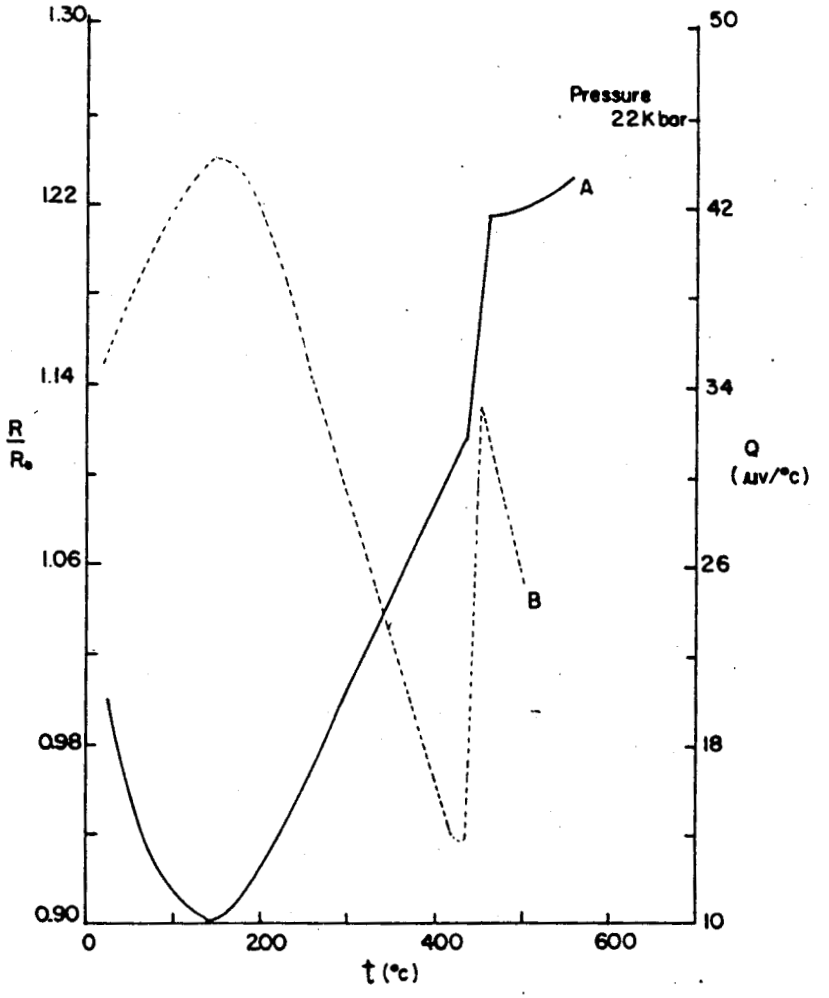

Fig. 7. R/R_0 (curve A) and TEP (curve B) as a function of temperature at 22 kbar.

METAL-SEMICONDUCTOR TRANSITION IN Yb

It is well known that Yb, a divalent rare-earth metal, undergoes a continuous metal-semiconductor transition around 13 kbar pressure due to the removal of the 6S-5d overlap. Extensive studies on this phase transition have been made (22). We present here some new data on TEP and resistivity obtained

under truly hydrostatic pressure conditions. Figure 6 gives a continuous record of relative resistance versus pressure at 25°C. It can be clearly seen that there is a change of slope near 12-13 kbar pressure which was not observable in all previous studies probably due to non-hydrostatic conditions. Also shown in the diagram is the TEP behaviour which manifests as a shoulder across the transition. The correlation of these data with the other electronic properties has been discussed elsewhere (11,12). In brief, the positive sign of Q is in conformity with the Hall effect data and the relatively large magnitude of Q is simply due to the small carrier concentration. The increase of Q with pressure in the semimetallic region is mainly due to the gradual removal of the band overlap and the consequent decrease in the electron concentration. In the semiconducting phase, the steep initial increase and the subsequent decrease in the magnitude of Q with pressure clearly point out to two opposing contributions to the electron diffusion TEP.

Figure 7 gives the temperature variation of the resistivity and TEP in the semiconducting phase of Yb. The main feature of the resistivity curve is the increase in resistivity with temperature above 150°C. It is to be noted that TEP in the same temperature region decreases linearly with temperature. These results strongly suggest that Yb behaves like a degenerate semiconductor (12) above 150°C.

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