

Critical phenomena in solids

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Abstract. In general a solid-solid phase boundary does not terminate in a critical point due to symmetry requirements. However, there exists systems like pure cerium metal and rare earth compounds like samarium sulphide where an isostructural solid-solid phase boundary terminates at a critical point. The critical point for the pressure-induced semiconductor-metal phase transition in SmS has been determined for the first time using the thermoelectric power data collected upto 12 kbar pressure and 850° C. These results are discussed on the basis of some theoretical models developed for the mixed valent compounds.

1. Introduction

The general feature of the phase-diagram of a substance is that the liquid-vapour phase boundary terminates at a critical point while a solid-solid phase boundary will either run to infinity or is intercepted by other phase boundaries. The existence of a critical point means that one can transform one phase to the other continuously without crossing the phase boundary. The main symmetry argument involved in the existence of a critical point is that the relevant phase transformation must involve only a quantitative change but no change of symmetry. For example, in the case of liquid-vapour critical point, both these phases are isotropic and lack long-range order. However in the general case of a solid-solid transition involving a symmetry change, it is impossible to conceive of a continuous phase transition whether or not there is a symmetry element. Thus the potential candidates to exhibit a solid-solid critical point are those elements or compounds which undergo an isostructural phase transition. The $v-a$ phase transition in cerium where the structure remains cubic is a classic example of a solid-solid phase boundary terminating at a critical point.

This paper is concerned with a special class of solid-solid phase transitions, *viz.*, isostructural electronic phase transformations like the $v-a$ transition in cerium and the semiconductor-metal transition in rare-earth monochalcogenides like SmS, SmTe and SmSe. We review briefly the extensive high pressure studies on the critical point phenomena in cerium and then discuss in some detail the recent experiments done in our laboratory to establish the critical point for the pressure-induced semiconductor-metal phase transition in SmS.

2. Some preliminaries

It is important for the present discussion to define precisely the meaning of the term 'continuous phase transformation'. The original classification of the order of phase transitions due to Ehrenfest envisaged only discontinuous changes in the appropriate derivatives of the Gibbs free energy. Thus a second-order phase transition corresponds to a discontinuous change in the second derivative of the Gibbs free energy (corresponding to quantities like specific heat, isothermal compressibility, etc.). However this type of classification is now considered inadequate in view of the experimental observation that in many situations quantities like specific heat actually diverges at the transformation temperature instead of a discontinuous change. The presently accepted classification scheme due to Fischer (1967) is very general and allows for both discontinuous and divergence of the derivatives of the thermodynamic potential. Thus by a continuous phase transformation, what we mean is that the first derivative of the Gibbs free energy is continuous across the transition while the higher order derivatives may be discontinuous or can diverge.

3. ν - α transition in cerium

Cerium, the first member of the rare earth series, undergoes an isostructural phase transition around 7 kbar pressure at room temperature. At room temperature and atmospheric pressure a well-annealed sample of cerium has the f.c.c. structure (ν -phase) whereas a cold-worked specimen is a mixture of the γ -phase and the β -phase which has a double hexagonal close-packed structure. However we will be mainly interested in the pressure behaviour of the γ -phase. Lawson and Tang (1949) from their high pressure x-ray diffraction work established that the phase transformation near 7 kbar involves only a decrease in the lattice parameter without any change in symmetry. That the isostructural γ - α transition is associated with the $4f$ - $5d$ electron promotion was suggested by Zachariasen (quoted by Lawson and Tang 1949) and independently by Pauling (quoted by Schuch and Sturdivant 1950).

A schematic energy band structure of the ν -Ce is shown in figure 1. The main feature of the electron structure is that a $4f$ level which is localised lies just below

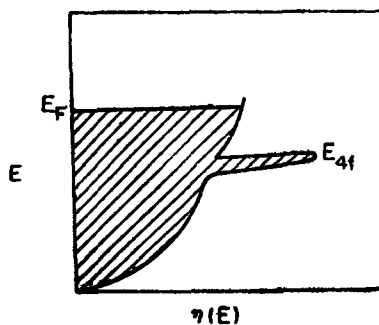


Figure 1. Schematic energy band structure diagram of ν -cerium.

the Fermi level (energy separation ≈ 0.05 eV). The conduction band is comprised out of the three $6s^2 5d^1$ electrons per atom. At the first order phase transition the $4f$ level shifts to a position above the Fermi level (in the model of Blandin *et al* 1965) or gets pinned to the Fermi level (Hirst 1970). The common feature of both these models is that in the α -phase there is a high density of states at the Fermi level due to the proximity of $4f$ virtual bound state.

An extremely interesting feature of cerium phase diagram (figure 2) is the termination of the ν - α phase boundary at a critical point. Beecroft and Swenson (1960) from their measurements on the lattice parameter decrease at various temperatures suggested that the discontinuity should disappear near 20 kbar pressure and 630° K. Jayaraman (1965) from his resistivity studies on cerium with pressure at various temperatures established the existence of a critical point at about 550° K and 17.5 kbar pressure. Figure 3 gives the various isotherms of the resistivity versus pressure. The magnitude of the resistance drop at the transition decreases with temperature and becomes continuous around 550° K, the critical temperature. Figure 4 gives the thermoelectric behaviour of cerium across the α - ν transition (Ramesh *et al* 1974a, b). These are isobaric curves and the transformation is studied by increasing the temperature. The temperature coefficient of thermopower is positive in the α -phase and changes sign in the γ -phase. The continuous phase transformation above the critical point is reflected in the general broadening of the curve, as can be seen in the isobars above 18 kbar pressure.

The resistivity behaviour just above the critical point deserves particular mention. A simple argument suggests that as the $4f$ virtual bound state sweeps through the Fermi level the resistivity should exhibit a maximum. The pressure at the resistivity maximum corresponds to the $4f$ level being right at the Fermi level. Some

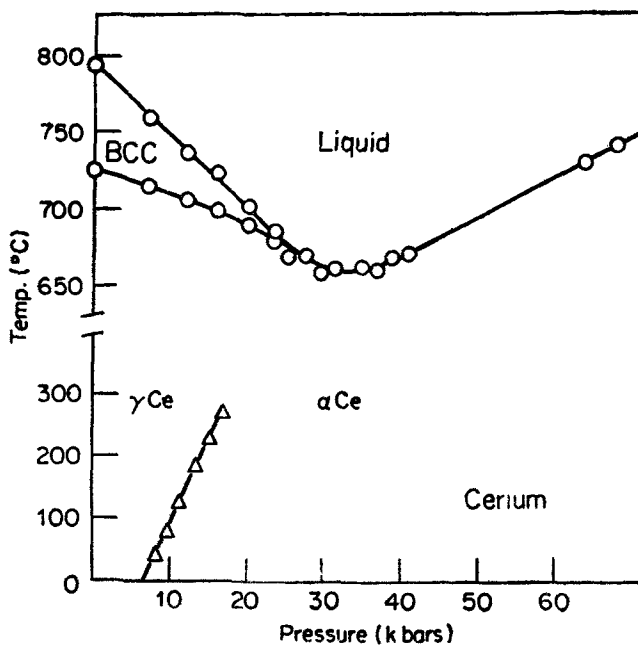


Figure 2. Phase diagram of cerium.

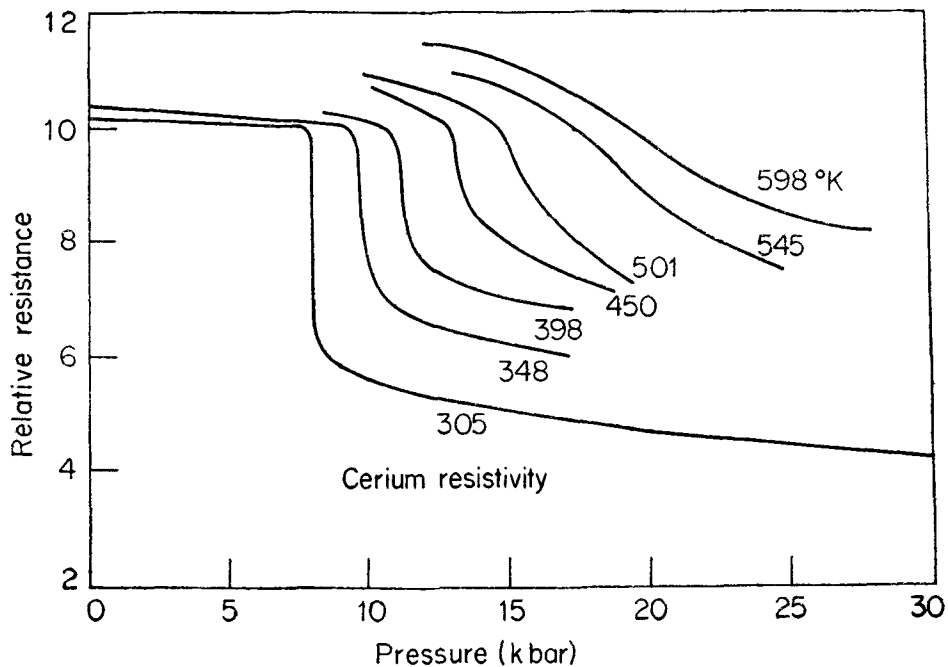


Figure 3. Isotherms of R vs P for Cerium.

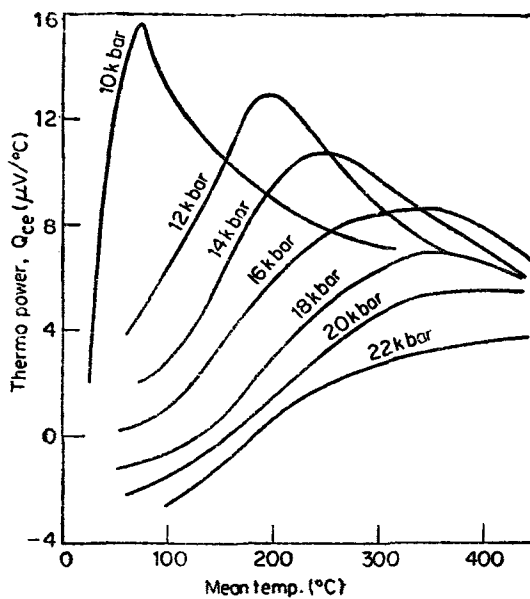


Figure 4. Isobars of Q vs T for cerium.

preliminary data on the resistivity behaviour close to critical point are given in figure 5 (Ramesh 1975). The decrease in resistance after 18 kbar is due to the

increase in the conduction electron concentration consequent to the $4f$ delocalisation as well as the vanishing of the spin disorder contribution to the resistivity. Detailed experimental results will be published elsewhere.

The behaviour of both resistivity and thermopower and other physical properties [magnetic susceptibility (Macpherson *et al* 1971), Hall effect (Gschneidner and Smoluchowski 1963) and specific heat (Gschneidner, 1965)] strongly support the model where the v - a transition is attributed to the $4f$ - $5d$ electron delocalisation. Further the fact that the slope of the v - a phase boundary is positive finds a simple explanation. In the v -phase, the Ce^{3+} ion core has the electronic configuration $4f^1$ with $J = 5/2$ as the ground state. However these localised spins are randomly arranged over the lattice (v -phase is paramagnetic) giving rise to a finite spin disorder entropy. The delocalisation of this singly occupied $4f$ level at the phase transition leads to the vanishing of this spin disorder contribution to the entropy. From the Clausius-Clapyron relation, viz, $dT/dP = \Delta V/\Delta S$, it is clear that the sign of dT/dP is mainly determined from those of ΔS because ΔV is always negative in a pressure experiment. If one hypothesises that the main entropy change at the phase transition is due to this delocalisation process (which makes ΔS negative), then it becomes clear that the slope of the T - P curve is positive. Although it is well established that there is a critical point for the v - a phase boundary, it is still not clear whether it is a simple critical point or a tricritical point. More experiments near the critical point specially the specific heat measurements are required to throw light on the nature of this critical point.

4. Critical point for $S \rightarrow M$ transition in samarium sulphide

Jayaraman *et al* (1975) discovered that SmS which crystallises in the NaCl-structure undergoes a strongly first-order isostructural phase transition near 6.5 kbar pressure at room temperature. This is a spectacular phase transition in the sense that the black semiconducting phase turns golden yellow at the transformation pressure. Further the high pressure phase of SmS like α -Ce exhibits such interesting behaviour as mixed valence (also known as fluctuating valence) anomalously large electronic specific heat, exchange enhanced susceptibility, etc. Since this discovery, many rare-earth chalcogenides like SmSe, SmTe, etc. at high pressures and compounds like SmB_6 , $Sm_{0.84}Gd_{0.16}S$, $Sm_{0.8}Th_{0.2}S$ at atmospheric pressure are found to

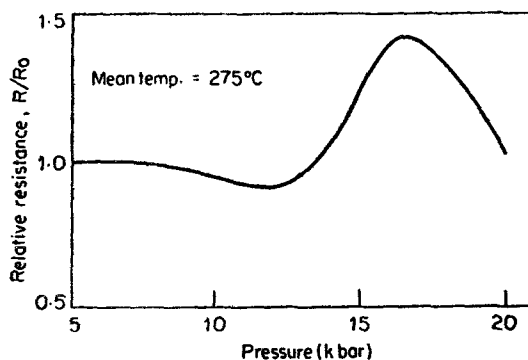


Figure 5. Resistivity behaviour near the critical point for cerium.

exhibit a similar behaviour. These studies have opened up the new field of mixed valence state, also known as the interconfigurational fluctuation state (ICF) wherein two ionic configuration states of the rare-earth ion, viz., $4f^n$ and $4f^{n-1}$ are degenerate at the Fermi energy. The present experimental situation has been reviewed by Maple and Wöhllben (1971) and the theoretical attempts to understand this phenomenon are summarised in the review by Varma (1976).

The present experiments on the thermoelectric behaviour of SmS across the semiconductor-metal transition were undertaken with the twin objectives of (i) establishing whether or not a critical point exists for the $S \rightarrow M$ transition in SmS and (ii) to study the thermopower, a sensitive electronic transport property, with pressure in the high pressure phase which exhibits several anomalies in other physical properties. A brief report of this work has been published elsewhere (Ramesh and Shubha 1976; Shubha *et al* 1978).

The experimental techniques for thermopower measurement at high pressures and high temperatures have been described elsewhere (Shubha and Ramesh 1976, Reshamwala and Ramesh 1974, 1975). Figure 6 gives the isotherms of the thermopower versus pressure. The data corresponding to 30°C was collected using the teflon cell technique with silicone fluid as the pressure transmitter. The high temperature data were collected using hexagonal boron nitride as the pressure transmitter. Great care has been taken to minimize the inhomogeneous pressure distribution over the sample by using very small samples ($\approx 0.5\text{ mm} \times 0.5\text{ mm} \times 0.2\text{ mm}$). The sharp discontinuity in the Q versus P graph at 530°C gives direct evidence of

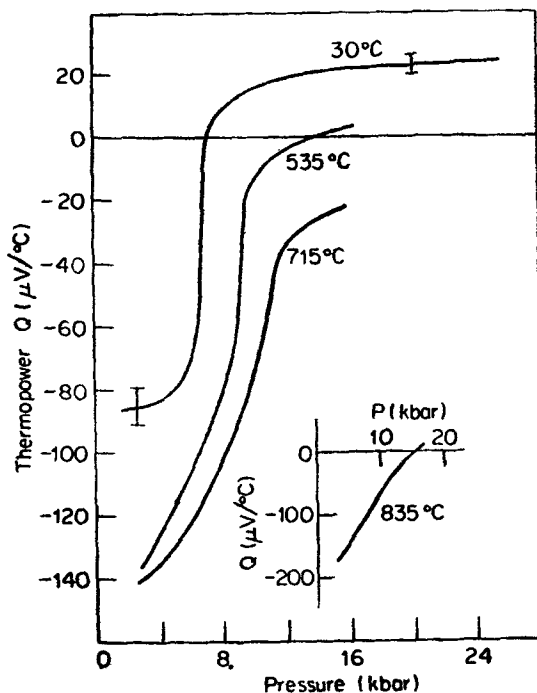


Figure 6. Isotherms of the Q vs P for SmS. Inset gives the isotherm at 835°C where Q is continuous with pressure.

the uniform pressure distribution over the samples. The experiments were performed with line pressure (which is the pressure of the hydraulic fluid before the intensifier) measurements accurate to ± 0.5 bar. Temperatures were maintained constant by slow variation and the accuracy in temperature measurements were $\pm 5^\circ\text{C}$. It is clear from figure 6 that the magnitude of the thermopower anomaly at the first-order phase transition decreases with increase of temperature. This behaviour is very similar to the one observed in the ν - α transition for Ce (Ramesh *et al* 1974). The isotherm at 715°C definitely shows the existence of the anomaly indicating that the critical point is above 700°C . The isotherm at 835°C (given in the inset) is continuous through the phase transition which gives direct evidence for the $S \rightarrow M$ phase boundary terminating in a critical point.

We have also used the progressive narrowing of the pressure hysteresis between the forward and the reverse transitions with increase in temperature as a criterion to track the critical point. Figure 7 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 reverse transition. It is clear that the difference in pressures at which the forward and reverse transitions occur (~ 5 kbar at 25°C) progressively narrows down at high temperatures. The temperature at which magnitude of thermopower anomaly vanishes and hysteresis interval closes down is around 825°C . We believe that the critical temperature for $S \rightarrow M$ phase boundary is around this temperature. Our data up to 835°C give for dT/dP a value of $170^\circ\text{C}/\text{kbar}$ which is considerably lower than the earlier estimates (Jayaraman *et al* 1975; Tonkov and Aptekar 1974).

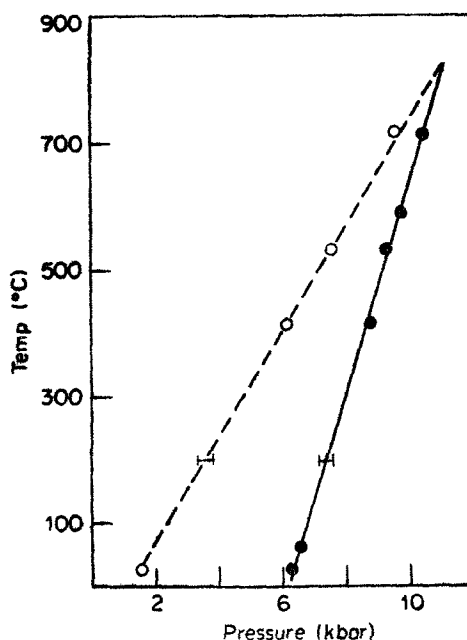


Figure 7. Phase diagram of SmS.

5. Discussion

Before considering the phase diagram of SmS and its relation to the mixed valence problem, we briefly discuss here the characteristics of the so-called 'intermediate valence state'. We consider the typical case of SmS. At atmospheric pressure, samarium is in the divalent state with the configuration $4f^6$. The conduction band of SmS is derived out of $6s$ and $5d$ states of the rare-earth ion and is empty at $T = 0$. The many electron $4f^6$ level is located close to the bottom of the empty $6s$ - $5d$ conduction band (energy separation $\simeq 0.065$ eV). The application of pressure causes the bottom of the $6s$ - $5d$ band to approach the $4f$ level, facilitating the promotion of an electron from the localised $4f$ state to the conduction band. At 6.5 kbar pressure and room temperature the $4f$ level moves abruptly into the conduction band leading to the semiconductor-metal transition. If we denote by ϵ , the energy necessary to make an interconfigurational excitation from $4f^n$ to $4f^{n-1}$ state (the other electron going over to the conduction band), then at the transition pressure ϵ goes from positive to negative values. Hirst (1970) proposed a model for the mixed valence state wherein $\epsilon \approx 0$. That is the $4f^n$ and $4f^{n-1}$ configurations gets 'locked-up' at the Fermi level as a consequence of several competing processes. It is clear that when ϵ is sufficiently small, the Anderson mixing interaction causes the individual ions to undergo spontaneous interconfigurational fluctuations by emission and absorption of conduction electrons. This fluctuation rate is of the order of Δ/\hbar where Δ is the width of the $4f$ virtual bound state. Since typically $\Delta \simeq 0.01$ eV, the characteristic time over which the individual ions undergo valence fluctuations turns out to be of the order of 10^{-12} sec. Since the ionic size in the two valence states vary considerably and if the lattice is unable to follow these rapid fluctuations, the system will stabilise with an "intermediate lattice parameter". Thus the lattice parameter is still the most direct and practical indicator of the intermediate valence state.

6. Static and dynamic models

There are two ways to visualise the mixed-valence state. In the static description, Sm ions are present as Sm^{2+} and Sm^{3+} ions. These distinct species are intimately mixed and completely disordered on an atomic scale. The valence does not fluctuate from one to the other state with time and stays static. In the dynamic picture, every Sm ion in the crystal fluctuates in time between Sm^{2+} and Sm^{3+} states on a rapid time scale—the relative time the electron spends in the two configurations determining the extent of intermediate valence. This dynamic description was fully developed by Hirst (1970) and is termed as the interconfigurational fluctuation (ICF) state.

To determine which model prevails over, we briefly go through the experimental evidence in this regard. (i) X-ray diffraction technique cannot differentiate between the static and dynamic pictures because it takes only a 'snap shot' of the structure. (ii) X-ray photo electron spectroscopic studies with a characteristic measuring time of 10^{-16} sec (which is less than the characteristic time of valence fluctuations) consists of the individual Sm^{2+} and Sm^{3+} spectrum which can be explained both in the static and dynamic models. (iii) The Mössbauer spectrum

with a characteristic time scale of 10^{-9} sec (which is much larger than the valence fluctuation time) however consists of a single line (Coe *et al* 1976). In the static picture one should expect two resonances and a single resonance line in the ICF model. Thus although these results seem to favour the ICF model, the experimental evidence is still inconclusive in view of the small shift (fraction of the line width) in the Mössbauer resonance frequency between Sm^{2+} and Sm^{3+} states.

The magnetic behaviour of these systems is puzzling and a clear understanding of this property is at the heart of the mixed-valence problem. If the Sm^{2+} ion after the phase transition had gone to a pure configuration state, then the Sm^{3+} state has a non-zero total angular momentum ($J = 5/2$). Then one would expect a Curie-Weiss behaviour at high temperatures and eventual magnetic ordering at low temperatures. However, experimentally the magnetic susceptibility is nearly flat in the low temperature regime and there is no evidence of magnetic ordering down to 1.3°K (Maple and Wohlleben 1971). But at higher temperatures a Curie-Weiss behaviour is observed. Maple and Wohlleben (1971) invoked the Hirst's model to qualitatively explain this strange magnetic behaviour. If we denote by T_f , the characteristic temperature for valence fluctuations ($T_f = \Delta/k$) the temperature dependence of the susceptibility in this situation has been proposed (Wohlleben and Coles 1973) to be of the form,

$$\chi(T) = \mu_{\text{eff}}^2 / 3k_B (T + T_f)$$

where $\mu_{\text{eff}}^2 = \mu_B^2 [\epsilon \mu_1^2 + (1 - \epsilon) \mu_2^2]$.

Here μ_1 and μ_2 are the magnetic moments of the nearly degenerate ionic configurations and ϵ is the fraction of time the electron spends in the local shell. For $T \gg T_f$ this reduces to the Curie-Weiss law, while at low temperatures it leads to a constant susceptibility.

All these experimental findings have a bearing on the phase diagram of SmS. Wio *et al* (1974) considered theoretically the phase diagram of SmS using a simple ionic model for the cohesive energy and included electronic terms similar to those of the Falicov-Kimball model for metal-insulator transitions. The theoretical predictions of this model are that the critical temperature is around 250°C and more over dT/dP turns out to be negative. It is worth pointing out that the authors have not considered the lattice contribution to the entropy which would be important at higher temperatures. Goncalves da Silva and Falicov (1975) have derived another equation of state for SmS which is a modification of the original Falicov-Kimball model and includes the effects of hybridisation between the localised and itinerant states. This theory again leads to a negative slope in the T - P plot. 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 interest. Since the high pressure phase of SmS exhibits a Curie-Weiss behaviour at higher temperatures implying that the Sm ions carry a magnetic moment, it is clear that there is a finite spin disorder entropy associated with the mixed valence phase. In contrast, the semiconducting phase with the ground state $J = 0$ has no spin disorder contribution. Thus if this is the only process involved in this phase transition, then dT/dP should be negative. It is not clear at present as to how important the lattice contribution is in this phase transition. Another problem of considerable experimental and

theoretical interest is that while SmS shows a discontinuous transition at room temperature, the closely related compounds SmTe and SmSe show a continuous phase transformation. The present thermopower study clearly establishes that even in SmS, the phase transformation is continuous above the critical point. A plausible explanation for the continuous transitions in SmTe and SmSe is that these systems have a lower critical temperature. Experiments at low temperatures and high pressures are required to confirm this point.

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