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ANOMALOUS TEMPERATURE DEPENDENCE OF THE THERMO-POWER IN THE HIGH PRESSURE PHASE OF CERIUM

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The thermo-electric behaviour of Cerium in the region lying below and above the critical point for the γ–α transition is reported. The anomalous temperature dependence and the continuous decrease of the thermo-electric power with pressure in the α phase are correlated with the models developed by Blandin *et al.* and Hirst.

THERE has been a considerable interest in the high pressure behaviour of Cerium and other $4f$ substances[1–7] like the rare-earth monochalcogenides. The high pressure phase of Ce and SmS possess such interesting properties as fractional valence, exchange enhanced susceptibility[6,7] etc. This behaviour has been attributed to the proximity of the $4f$ virtual bound state to the Fermi level.[2,4]

Among the transport properties only the resistivity behaviour of Cerium has been studied at high pressures.[1] In this note we report some new data on the thermo-electric behaviour of Cerium at high temperatures and high pressures. The important findings of this study are (1) a significant variation in the magnitude of the thermo-power in the low pressure region of the α phase and (2) a drastic decrease in the rate of variation of thermo-power with temperature at higher pressures. Our results support the view that in the low pressure region of α–Ce, the $4f$ virtual bound state is just above the Fermi level ($\sim kT$) and moves further apart at higher pressures.

Earlier we have reported[8] on the variation of thermo-power of γ–Ce with pressure in the temperature range 10–100°C using a teflon thermo-power cell developed in our laboratory.[9] In the present investigation we have scanned the γ–α phase transition in the region both below and above the critical point. These results were obtained using a high temperature and high pressure thermo-power cell, the details of which will be described elsewhere.[10]

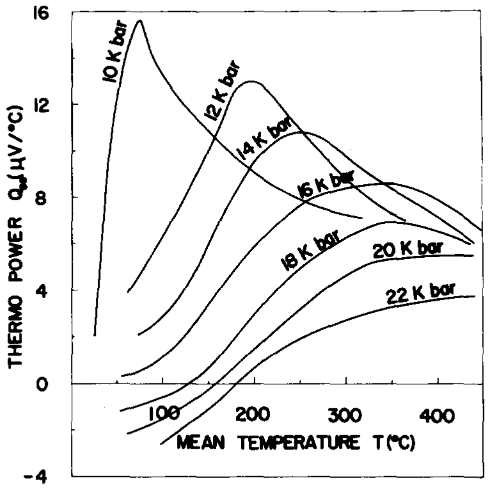

FIG. 1. Thermo-power vs temperature data at different pressures.

Figure 1 presents a set of isobaric curves showing the α–γ phase transition as studied through thermo-electric power. The temperature coefficient of thermo-power 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 most interesting feature of these isobaric curves is the dramatic increase in the thermo-power with temperature in the α phase. The isobar at 10 kbar

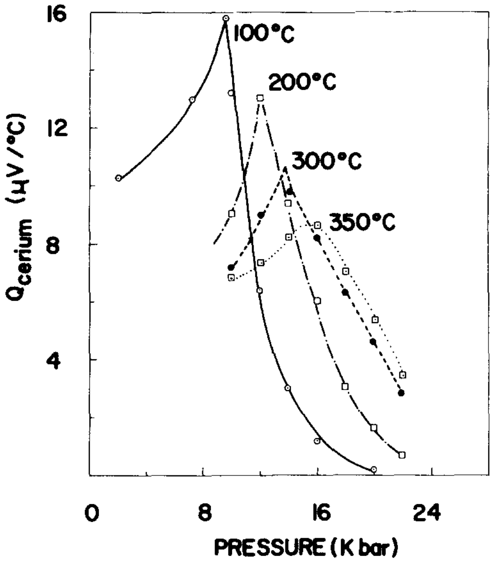

FIG. 2. Isotherms of the thermo-power vs pressure graph.

pressure, in particular, shows that over a small temperature range of 25°C, the thermo-power (Q) increases from nearly $+2\mu V/^{\circ}C$ to $+10\mu V/^{\circ}C$ i.e. dQ/dT is nearly $+0.35\mu V/^{\circ}C$.[2] One can expect that the isobars corresponding to pressures lower than 10 kbar and transition temperatures lower than 0°C will be characterized by a much steeper increase of thermo-power with temperature. It is interesting that this rate of increase decreases markedly at higher pressures. For example, dQ/dT at 20 kbar pressure is nearly $+0.03\mu V/^{\circ}C$,[2] which is about 10 times smaller than that at 10 kbar pressure.

Figure 2 presents the thermo-power vs pressure isotherms constructed out of the data in Fig. 1. It can be seen from the diagram that the magnitude of the anomaly associated with the γ–α transition decreases as the temperature is raised, which is quite similar to the resistivity behaviour. The isotherms at 100 and 200°C exhibit a near vertical drop at pressures corresponding to the first order γ–α phase transition. However the isotherm at 300°C has a smooth behaviour characteristic of the continuous phase transformation above the critical point.

The following discussion is based on the theoretical model developed by Blandin *et al.*[2] and Hirst[4] for α–Ce. Experimental evidence such as the Hall effect measurements on γ and α–Ce,[11] magnetic susceptibility measurements at high pressures,[6] absence of superconductivity in the α–Ce[12] etc. suggest that the $4f$ level in α–Ce is located just above the Fermi level at lower pressures and moves further apart at higher pressures. In the Hirst's model,[4] the $4f$ virtual bound state gets "locked up" with the Fermi level over a finite pressure region and such a thermodynamic state possesses rather unusual properties. Since the excitation energy for the configurational cross-over from $4f^1$ to $4f^0$ is zero (when the virtual bound state is locked to the Fermi level), the individual ions undergo rapid interconfiguration fluctuations by emission and absorption of conduction electrons with a fluctuation rate of order $\Delta/\hbar$, Δ being the width of the $4f$ virtual bound state. Further for temperatures $kT < \Delta$ ($\Delta \approx 10^{-2}$ eV), the ionic configuration is fairly well defined whereas at higher temperatures viz. $kT > \Delta$, the system should be described by a weighted average of the two configurations. It is important to note that the delocalization of nearly one electron per cerium ion should cause a dramatic increase in the Fermi energy. The different isotherms of the occupancy of the $4f$ state in the α phase as a function of the parameter $(E_{4f} - E_F)$ given by Blandin *et al.*[2] shows that there is a considerable excitation of the conduction electrons to the $4f$ state (lying just above the Fermi level) at high temperatures.

The anomalous temperature dependence of the thermo-power in the low pressure region of the α-phase can be qualitatively understood on the basis that both the variation of the conduction electron density and the energy dependence of the relaxation time are important. The existence of a resonant state just above the Fermi level causes the scattering cross-section to vary markedly with temperature. When $E_{4f} - E_F$ is of the order of kT, the $4f$ level characterized by a high density of states, provides the alternative states for scattering for the current carrying conduction electrons. The scattering cross-section thus increases rapidly with temperature and this leads to $[d\tau(E)/dE]_{E_F}$ becoming strongly negative at higher temperatures. Thus the contribution of this factor to the thermo-power is positive. The decrease in the conduction electron density owing to the partial excitation into $4f$ states has the effect of enhancing the magnitude of the thermo-power. This is because the thermo-power is inversely related to the number density of mobile electrons. The electrons in the $4f$ state have much lower mobility and may be expected not to contribute directly to the electron diffusion process. The decrease in the rate of variation of thermo-power with temperature at higher pressures finds a simple explanation. In this pressure region, the $4f$ state has moved sufficiently away from the Fermi level. Then the conduction electron density varies little with temperature. The energy dependence of the relaxation time would also be weaker when the resonant state lies significantly above the Fermi energy. It would be of great interest to study the thermoelectric properties of the high pressure phase of SmS which is also expected to show a similar behaviour.

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Le comportement thermoélectrique du cérium dans la région inférieure et supérieure au point critique pour la transition de γ–α est donne. La dépendance température anomal et l'abaissement continu de la puissance thermoélectrique avec la pression dans la phase α correspondent aux modèles developées par Blandin *et al.* et Hirst.