LOW-TEMPERATURE HEAT CAPACITY OF α - AND β -CERIUM*

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Both the β and the α phases of Ce are present in samples of the metal at low temperatures. The β phase is essentially trivalent, and has one localized 4f electron. The α phase has a valence intermediate between 3 and 4. The fourth electron is no longer in a well localized 4f state,¹ nor is it fully promoted into the conduction band. The valence usually assigned² to the α phase is 3.6.

We have measured the heat capacities of mixed-phase samples of different compositions and have extrapolated the data to the pure phases using the magnetic ordering anomaly in the β phase as a measure of the composition. The standard technique of thermal cycling was used to increase the mole fraction of the β phase, χ_β , and measurements were obtained on samples whose χ_β ranged from 0.3 to 0.8. The heat capacity observed in experiment i can be represented by $C_i(T) = \chi_{\beta_i} C_\beta(T) + (1 - \chi_{\beta_i}) C_\alpha(T)$, where C_β and C_α are the heat capacities of the pure β and pure α phases. (This equation neglects the small, χ_β independant peaks in the heat capacity near 0.15, 0.9, and 6 K. These peaks are sample dependent and probably are impurity

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related. They do not significantly interfere with the determination of χ_{β} .) C_{α} can be extrapolated from the mixed phase data through a series of trials in which different ratios of χ_{β_i} 's are assigned to the observed C_i 's. The correct ratio gives a C_{α} which varies smoothly through the 12.5 K region of the β phase's anti-ferromagnetic ordering peak. This C_{α} agrees with the C_{α} measured by Panousis and Gschneidner³ at low temperatures. Above approximately 6 K, their sample has an anomalously high heat capacity which cannot be ascribed entirely to the approximately 3% β phase present. Panousis and Gschneidner have also reported the heat capacity of a sample for which χ_{β} was measured dilatometrically⁴ to be 0.91 ± 0.05 . From this C_i and from C_{α} the χ_{β_i} 's of other experiments and C_{β} can be determined.

The value of γ , 22 mJ/mole·K², obtained for α Ce is appreciably higher than expected for a metal with a purely s-d conduction band and a valence of 3.6. The excess is attributable to the presence of the 4f electron in a state which overlaps the Fermi surface, and is of the order of magnitude predicted by the virtual bound state model.⁵ By 10 kbar, γ has decreased⁶ to 11.3 mJ/mole·K². This decrease reflects the increase in energy of the f state relative to the Fermi surface.

The θ_0 of α Ce is approximately 125 K, lower than the estimated 150 K θ_0 of β Ce,⁷ in spite of the 17% greater density⁸ and the higher valence of α Ce.

At low temperatures the heat capacity of β Ce can be represented by $C_{\beta} = 54 T + 5.6 T^3$ mJ/mole-K and is field independent to at least 60 kOe.

The T^3 term is an order of magnitude higher than expected for the lattice heat capacity. It is consistent with a spin wave heat capacity in the absence of an anisotropy field, but in that case it should be substantially reduced by a 60 kOe external field. The linear term is unusually high and is 5 times higher than would be expected for β Ce on the basis of its similarity to La. Large linear terms occur for other magnetic rare earths at low temperatures but at room temperature the linear terms all have the lower values found in nonmagnetic rare earths, as shown in table 1. These facts suggest the importance of a temperature dependent magnetic enhancement of the electronic heat capacity.

The entropy associated with the 12.5 K antiferromagnetic ordering peak of β Ce is approximately $1/2 R \ln 2$, indicating that only half of the localized 4f electrons order at that temperature. Beta Ce has a double hexagonal close packed structure, with half of the atoms in a cubic and half in a hexagonal environment, and it is not surprising that atoms on different sites do not order at the same temperature. The neighboring rare earths Pr and Nd also have this structure. The hexagonal sites of Nd¹⁰ order at 19 K and the cubic ones at 7.5 K. Only the hexagonal sites of Pr order¹¹ at 25 K. Judging from the trend in transition temperatures, it is the cubic sites which order in β Ce at 12.5 K.

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FIGURE CAPTIONS

- Figure 1 The low temperature heat capacity of Ce.
- Figure 2 The high temperature heat capacity of Ce.
- Figure 3 The effect of a 60 kOe field on the low temperature heat capacity of Ce. The LU and RC samples are from different suppliers.

TABLE I
Properties of the Rare Earths

	γ_{300} (mJ/mole K)	apparent γ_o^d (mJ/mole K)	T_N^i (K)	T_C^i (K)	low temperature magnetic structure
La		9.4 ^e	---	---	none
Ce	7.5 ^c	54 ^f	7, 12.5	---	complex antiferromagnetic
Pr	7.3	26.2	25, ---	---	complex antiferromagnetic
Nd	8.6	58	20, 7.5	---	complex antiferromagnetic
Sm	11.5	12.4	14.8	---	complex antiferromagnetic
Eu ^a	3.7	12.1	90	---	complex antiferromagnetic
Gd	9.2	(11) ^g	292	293	simple ferromagnetic
Tb	12.2	10.4	229	221	simple ferromagnetic
Dy	9.1	17.9	178.5	85	simple ferromagnetic
Ho	7.9	50	132	20	conical ferromagnetic
Er	11.8	(9.1) ^h	85	19.6	conical ferromagnetic
Tm	7.2	22.3	51-60	22	complex ferrimagnetic
Yb ^a		2.9	---	---	none
Lu		11.3	---	---	none

^a divalent; the rest are trivalent

^b reference 12

^c fcc γ phase

^d reference 13 except as noted

^e reference 14, dhcp phase

^f present work, dhcp β phase

^g reference 15, not recalculated.

^h reference 16, not recalculated.

ⁱ reference 17

XBL 725-6227

Figure 1

XBL 725-6229

Figure 2

XBL 725-6236

Figure 3