The heat capacity of β-cerium between 1.5 and 23 K

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The heat capacity of single-phase β-cerium has been determined between 1.5 and 23 K with special emphasis on the shape of the antiferromagnetic ordering peak. It is concluded that separate ordering occurs at 12.45 and 13.7 K for the two types of site symmetry. The lower-temperature peak is thought to be associated with ordering of the cubic sites and the upper peak with the ordering of the hexagonal sites. An analysis of the various contributions to the heat capacity is made. The magnetic heat capacity between 1.5 and 2.3 K exhibits an exponential behavior, yielding an energy gap of 2.92 K, and between 3.5 and 6.5 K it exhibits a T^3 behavior.

It is well established from neutron diffraction[1] and magnetic-susceptibility measurements[2] that the double hexagonal close-packed (dhcp) β-allotrope of cerium is antiferromagnetic below 12.5 K. Heat-capacity measurements[3–5] show a magnetic-ordering peak at this temperature. However, it has been difficult to obtain more detailed information from heat-capacity measurements below 20 K because uncertainties in the crystal-field levels and their associated Schottky anomalies make it difficult to resolve the other contributions to the heat capacity. The magnetic contribution, especially, has been the subject of disagreement. Some uncertainty can also be attributed to the fact that until now all physical-property measurements for the β-phase have been made on mixtures of β with at least 9% α- or γ-cerium.

Recently we have found a way to prepare at least 99.5% β-cerium containing no detectable amounts of either α- or γ-cerium by a process of successive quenching and annealing steps.[6] The heat-capacity results reported here were made on a 39.4-g single-phase β-sample prepared in this way. This same sample was later given to C. J. Stassis of this Laboratory who made some elastic and inelastic neutron scattering measurements on it. The neutron diffraction pattern showed only β-cerium lines and the inelastic scattering data indicated the energies of the crystal-field levels. Our specific-heat measurements have been interpreted in light of his results.

EXPERIMENTAL PROCEDURE

The cerium used in this investigation was prepared at Ames Laboratory and is believed to have a higher purity (99.87 at. %) than that used in any previous investigation. The analysis of this metal is given in Table I.

The experimental details of the preparation of single-phase β-cerium are reported elsewhere.[6,7] Briefly, single-phase γ-cerium was thermally cycled between room temperature and 4.2 K ten times and annealed at 75 °C for one week. This process of thermal cycling and annealing was repeated four times.

The heat capacity was measured using an adiabatic calorimeter with an accuracy of 1% above 3 K and about 2% below 3 K. Further details on this apparatus are found elsewhere.[7]

RESULTS AND DISCUSSION

The heat-capacity results[8] are illustrated in Fig. 1. The most prominent feature of these data is the antiferromagnetic ordering peak centered at 12.45 K. The peak is sharper than the peaks reported by Panousis and Gschneidner[4] and by Conway,[5] and reaches a higher value as would be expected on the basis of the higher percentage of the β-phase. Probably the annealing treatments given our sample helped to relieve much of the lattice strain which is present in their samples by nature of the quenching methods they used to form β. These lattice strains would tend to smear out the ordering peak.

In addition to the ordering peak at 12.45 K there is a bump at 13.7 K. This bump could be a second peak similar to the first. Since the high-temperature side of an ordering peak is steeper than the low-temperature side, two peaks close to each other, when added together, can appear as one peak with a shoulder rather than two individual peaks. We believe that these two peaks correspond to separate antiferromagnetic ordering temperatures for the two types of lattice sites in β-cerium. Current studies on β-cerium show evidence for two peaks in the magnetic susceptibility and electrical-resistivity measurements. The atom sites for the dhcp structure are equally divided between sites with cubic and hexagonal symmetries as can be immediately concluded from the *ABAC* packing sequence of close-packed planes. The atom sites in the *A* layers have a fcc-type nearest-neighbor environment while those in the *B* and *C* layers have an hcp environment. Neodymium and samarium also have both cubic- and hexagonal-site symmetries and, like cerium, con-

TABLE I. Chemical analysis of cerium used (impurity levels are in atomic ppm).

Impurity	Ce(I)	Impurity	Ce(I)
H	139	Ag	< 0.05
N	90	Cd	< 0.1
O	639	In	< 0.08
C	152	Sn	< 0.4
F	111	Sb	< 0.08
Li	< 20	Te	< 0.1
Be	< 0.1	I	< 0.1
B	0.1	Cs	< 1
Na	10	Ba	< 10
Mg	< 0.4	Hf	< 6
Al	1	Ta	7
Si	1	W	< 0.3
P	< 2	Re	< 0.8
S	0.5	Os	< 1
Cl	8	Ir	< 0.8
K	5	Pt	0.5
Ca	20	Au	< 0.1
Ti	< 2	Hg	< 0.2
V	< 0.5	Tl	< 0.1
Cr	15	Pb	< 2
Mn	< 1	Bi	< 0.08
Fe	7.5	Th	0.4
Co	< 0.1	U	< 0.2
Ni	3	Sc	1
Cu	3	Y	5
Zn	< 1	La	34
Ga	•••	Pr	5
Ge	< 4	Nd	8
As	< 0.2	Sm	< 0.07
Se	•••	Eu	< 0.05
Br	< 0.4	Gd	< 1.2
Sr	•••	Tb	< 0.2
Zr	< 0.9	Dy	< 0.1
Nb	•••	Ho	< 0.3
Mo	< 1	Er	1.6
Ru	< 1	Tm	< 0.05
Rh	< 0.2	Yb	< 0.05
Pd	< 1	Lu	9

sist of Kramers type (J = half-integer) magnetic ions. Both of these elements have separate antiferromagnetic ordering temperatures for their two types of sites, with neodymium[9] ordering at 7.5 and 19 K and samarium[10] at 14 and 106 K. But for these two metals separate ordering peaks are observed[11,12] since their ordering temperatures are far apart relative to that of β-cerium. In addition Roberts and Lock[13] found that the 12.5-K peak in cerium splits into two readily observable parts when lanthanum is added to cerium, but in contrast yttrium additions[4] bring these peaks together, sharpening the shape of the heat-capacity ordering peak. The reason two peaks have not been previously detected in pure cerium is probably due to the aforementioned broadening or smearing together of the peaks by lattice strains.[14]

Crystal-field studies are not as common for the rare-earth metals as for rare-earth salts because the exchange interaction dominates the crystal-field interaction in the metals. In β-cerium the situation is complicated further by the existence of two lattice-site symmetries. The perturbing effect two types of site symmetry may have on the crystal-field levels of one another has never been calculated, and thus far the two symmetries have been assumed independent. From Kramers rule it follows that the maximum crystal-field splitting of the $^2F_{5/2}$ ground-state level of the Ce^{3+} ion is into three doublets. It is well established that a cubic crystal field results in a ground-state doublet with an excited quartet while a hexagonal field results in three doublets. The excitation energy of the quartet has been calculated to be 206 K by Murao and Matsubara[15] and 270 K by Bleaney.[16] The excitation energies of the doublets have been calculated to be 30 and 150 K by Bleaney, but the value of 30 K has been disputed by specific-heat

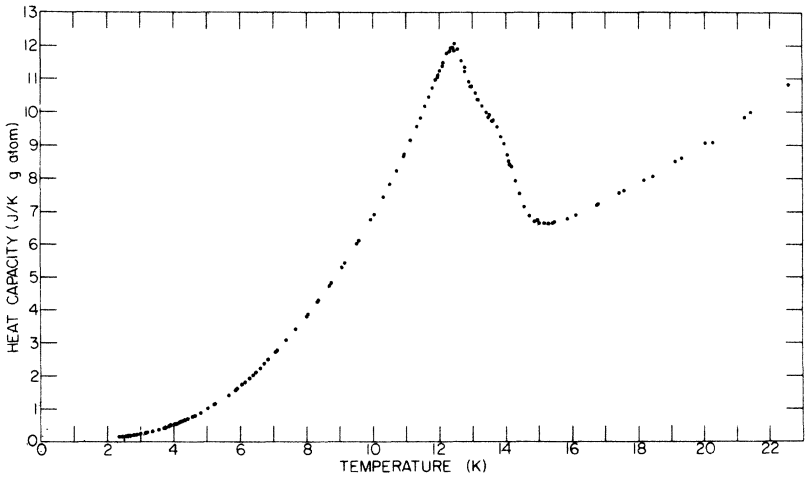

FIG. 1. Heat capacity of β-cerium from 2 to 23 K. The data points below 2.3 K are not shown.

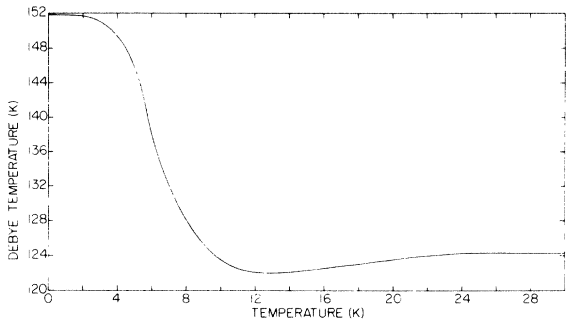

FIG. 2. Debye temperature of cerium, assuming it is the same as that of lanthanum.

measurements.[4] Yoshida and Sugawara[17] have calculated values of 89 and 206 K for the doublets of Ce^{3+} ions in hexagonal yttrium, but these values may not be applicable to pure cerium. Panousis[18] experimentally estimated the two doublets to lie 85 and 110 K above the ground state on the basis of an analysis of the low-temperature heat capacity of cerium-rich Ce-Y alloys. More recently neutron inelastic scattering on pure β-cerium performed in this Laboratory[19] indicated the presence of crystal-field levels at 98, 113, and 206 K. The 98- and 113-K levels have been assumed to be the excitation energies of the two doublets and the 206-K level to be the excitation energy of the quartet. Using these values we have calculated the Schottky contribution to the heat capacity.

A determination of the electronic and lattice specific-heat contributions is complicated by the existence of the antiferromagnetic ordering peak.

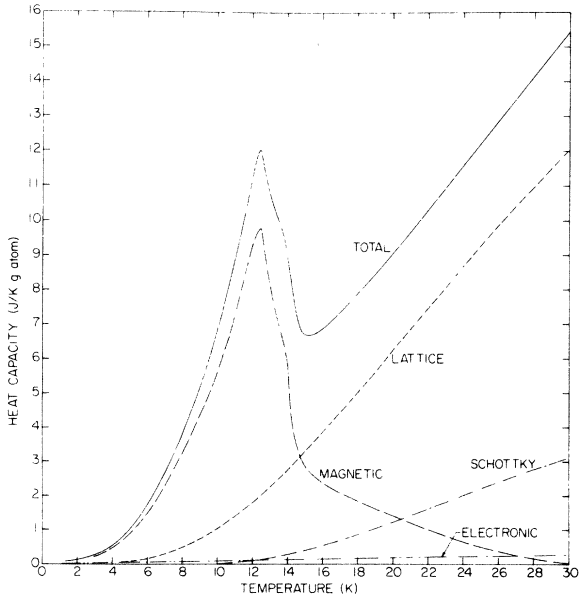

FIG. 3. Various contributions to the heat capacity of β-cerium.

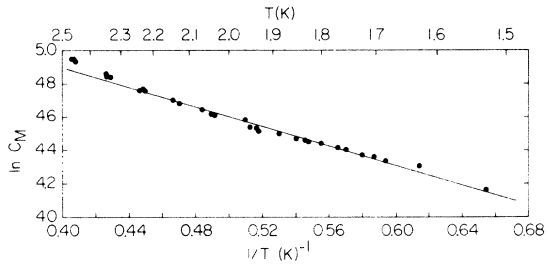

FIG. 4. Logarithm of the magnetic heat capacity vs the reciprocal of the temperature. The actual data points from which the electronic and lattice contributions have been subtracted are presented here. The units for C_M are mJ/K *g* atom.

Below 3 K a C/T vs T^2 curve tends to curve upward from a straight line drawn from higher temperatures. If this curve is extrapolated to the C/T axis, the intercept gives an electronic specific-heat constant of 46 ± 2 mJ/g atom $°K^2$ which seems anomalously high. Since α-lanthanum is very similar to β-cerium in all properties other than those associated with the 4*f* electron in β-cerium, the electronic specific-heat constant (9.4 mJ/g atom $°K^2$) and Debye temperature of α-lanthanum[11,20] can be used to a good approximation for β-cerium. The temperature dependence of the Debye temperature of α-lanthanum is illustrated in Fig. 2. Subtracting the lattice, electronic and the Schottky contributions from the total heat capacity gives the magnetic contribution. Figure 3 illustrates these contributions.

The magnetic heat capacity which results has a measured magnetic entropy to within 1% of the theoretical value of $R \ln 2$ which would be expected for a doublet ground state. The shape of this peak (Fig. 3) with its rather long high-temperature tail and break around 15 K, is similar to that found for

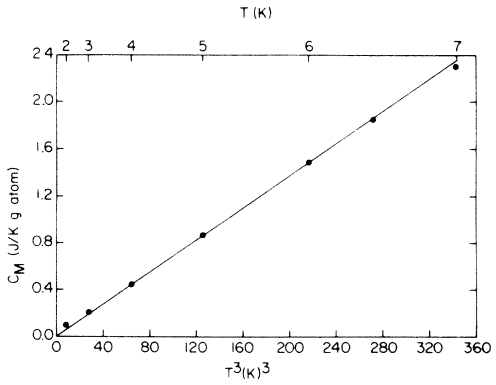

FIG. 5. Magnetic heat capacity vs the temperature cubed. The data points are taken from a smoothed curve of *C* vs *T* and from which the electronic and lattice contributions have been subtracted.

samarium,[12] whose tail extends out to $\sim 2T_N$, which is about the same extent as the β-cerium tail.

Various temperature dependences have been predicted by theorists for the magnetic contribution to the heat capacity, C_M, below the ordering temperature. In the spin-wave approximation

$$C_M = DT^n, \tag{1}$$

where D is a constant and $n = \frac{3}{2}$ for a simple ferromagnet and $n = 3$ for a simple antiferromagnet.[21] Magnetic anisotropy introduces an energy gap, Δ/k, and gives rise to equations of the form

$$C_M = f(T)\, e^{-\Delta/kT}, \tag{2}$$

where $f(T)$ is a complicated function and is dependent on the nature of the spin-wave spectrum.[22-24] Furthermore, Cooper[22] and Mackintosh[23] noted that for temperatures below the energy gap an equation of the form of (2) is expected to hold,[25] but for temperatures greater than Δ/k Cooper[22] predicted an equation of the form of (1) should be followed with $n = 1$.

An analysis of the low-temperature portion (<7 K) of the magnetic heat capacity of β-cerium does indeed show an exponential temperature dependence below Δ/k and a T^n behavior above it. A plot of $\ln C_M$ vs $1/T$, which is given in Fig. 4, shows that the exponential temperature dependence is followed from our lowest-temperature data point (1.5 K) to between 2.3 and 2.4 K, where a clear departure is seen to begin. The line drawn through the points in Fig. 4 is a least-squares fit of the data, and the fit yields an energy gap of 2.92 ± 0.06 K and a constant of proportionality of 428 ± 12. It is interesting to note that the term $f(T)$ in Eq. (2) is a constant (428) and not a complicated function of temperature as predicted by theory. Although the fit of the data holds up to about $0.8\ \Delta/k$, much higher than Cooper's theory seems to apply,[25] the analyses of Morrison and co-workers[26,27] show that Eq. (2) holds up to at least $0.9\ \Delta/k$ for Pr and Nd. The value of the energy gap is in very good agreement with the results of Morrison and co-workers[26,27] who derived values ranging from 2.44 to 3.0 K from the heat capacities of Pr, Nd, Eu, and Tm, but different from those reported by Lounasmaa and Sundström[28] who derived values of 0 K (no energy gap) for Gd, Ho, and Tm and 23.5 and 31 K for Tb and Dy, respectively.

At temperatures above the energy gap the magnetic contribution to the heat capacity is found to obey a T^3 law up to $\sim \frac{1}{2} T_N$ (see Fig. 5). An analysis of the data between 3.5 K ($T^3 = 42.9$ K^3) and 6.5 K ($T^3 = 272$ K^3) gives a slope of $(6.9 \pm 0.1) \times 10^{-3}$ J/g atom K^4, which is slightly larger than the value (6.5×10^{-3}) found by Panousis and Gschneidner.[4] This suggests that in this temperature range the magnetic contribution of β-cerium follows simple spin-wave theory.

The observation of two different temperature behaviors for the magnetic heat capacity of β-cerium, one being exponential and the other being nonexponential, is consistent with Cooper's theory.[22] But the observed detailed dependencies are significantly different from prediction. Apparently this is the first time that the magnetic heat capacity of a rare-earth metal was found to have two different temperature dependences.

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