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Zero-field and magnetic-field low-temperature heat capacity of solid-state electrotransport-purified erbium

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Zero-field (1.5–80 K) and high-magnetic-field (1.5–20 K) low-temperature heat-capacity measurements have been carried out on 99.97 at. % (99.996 wt %) pure polycrystalline erbium. The electronic specific-heat coefficient (in zero field) was found to be 8.7 ± 0.1 mJ/mol K^2 and the Debye temperature to be 176.9 ± 0.4 K. The "ferromagnetic" transition of erbium around 19 K exhibits a tremendously large and sharp heat-capacity maximum of 169 J/mol K. Five other heat-capacity anomalies at 25.1, 27.5, 42, 48.9, and 51.4 K were observed. The 51.4-K peak is associated with antiferromagnetic ordering in the basal plane, and the other four anomalies are associated with spin-slip transitions between two different commensurate antiferromagnetic structures. An external magnetic field shifts the ferromagnetic heat-capacity peak toward higher temperatures with a remarkable suppression and broadening of the maximum, and reduces the total heat capacity below the magnetic ordering maximum for temperatures down to about 5 K. At lower temperatures, the high-magnetic field ($H > 5$ T) increases the sample heat capacity due to an increase in both the ^{167}Er hyperfine coupling and electronic contributions. The effective magnetic field at the nucleus increases from 7.2 MOe at $H=0$ to 10.3 MOe at $H=9.85$ T. The electronic specific constant (density of state at the Fermi level) exhibits a 15% increase at $H\sim2$ T due to a spin reorientation of the basal plane moments. This change is also evident in the magnetic contribution to the heat capacity.

I. INTRODUCTION

The heat capacity of metallic erbium was studied by Skochdopole, Griffel, and Spedding[1] over a relatively wide temperature region from 15–320 K. Subsequently others[2–8] measured it at low temperatures down to 0.03 K. All investigations except the ones carried out by Hill, Cosier, and Hukin[6] ($0.4 \text{ K} < T < 23$ K) and Schmitzer *et al.*[7] ($1.7 < T < 60$ K) were made on dirty (compared to what is available today) materials. And even Hill, Cosier, and Hukin and Schmitzer *et al.* did not give any chemical analyses for their erbium samples. Hill, Cosier, and Hukin[6] purified their erbium samples by zoning and noted that the residual resistance ratio varied from 38 to 54 for four different samples. Schmitzer *et al.*[7] measured the heat capacity of three erbium samples, one of which was of a poor quality, and one that had been purified by zoning, however no other details were given. The third sample of Schmitzer *et al.*, which they identified as "Johnson-Matthey", was probably the purest of the three by virtue of the higher peak height of the 19 K magnetic transition and the sharper transitions at 28 and 53 K. Any further reference to the heat capacity of Er of Schmitzer *et al.* will be made with respect to the Johnson-Matthey material. From the peak height and peak width of the 19 K magnetic transition, the samples of Hill, Cosier, and Hukin are probably purer than any of the samples of Schmitzer *et al.*, and for this reason, for the most part, we will compare our results with those of Hill, Cosier, and Hukin. As a result of these eight studies, heat-capacity anomalies have been reported at 84, 53.5, 28, and ∼19 K.

Early neutron-diffraction studies[9–11] showed that pure erbium undergoes three magnetic phase transitions at $T_{N_\parallel}=84$ K [from paramagnetic to a *c*-axis modulated (CAM) structure], $T_{N_\perp}=53$ K [from the CAM structure to an antiphase domain (APD) cone plus helix structure] and $T_c=18$ K [from the APD cone plus helix structure to a ferromagnetic cone plus helix structure], plus an inflection point in the temperature dependence of the modulation vector at 33 K and a lock-in transition at 24 K. More recently Gibbs *et al.*[12] using x-ray synchrotron radiation and neutron-scattering measurements found a sequence of lock-in transitions to rational wave vectors, which are called spin slips. Subsequently three groups have studied these spin-slip transitions by a variety of techniques: high-resolution scanning microcalorimetry,[13] ac magnetic susceptibility,[14,15] magnetization,[16,17] thermal expansion[17] and electrical resistivity,[15] and neutron scattering.[18] The reported structure changes take place at approximately 51, 40, 34, 29, 27, and 20 K.

Since the heat capacity is an extremely sensitive property, which reflects notably all of the phase transitions occurring in a bulk material, including such delicate ones as mentioned in the above paragraph, and, since we have purifying techniques that offer really high-purity materials, we have chosen to investigate a polycrystalline erbium sample prepared by Fort, Beaudry, and Gschneidner[19] by using solid-state electrolysis (also called electrotransport purification). This sample is probably the highest purity polycrystalline erbium sample ever prepared. Another reason to carry out this study was that only one anomaly (at 28 K) had been observed in the previous heat-capacity measurements between 19 and 52 K (Ref. 7) (most of the other studies[2–6] never exceeded 23 K).

II. EXPERIMENTAL PROCEDURES

A rodlike erbium specimen about 7 mm in diameter and 10 mm long was cut off from the cathode section of the electrotransport-purified material as described by Fort, Beaudry, and Gschneidner.[19] The results of detailed chemical analyses show that the impurity contents were as follows (in ppm atomic): C-111, O-168, F-44, Na-3.8, K-1.8, Fe-2, Cu-1.6, Ho-3.7, Ta-1.3, and Pb-2. The amounts of other contaminants were below limits of detection (i.e., less than 1 ppm). This gives a total impurity content of 338 ppm atomic, i.e., a purity of 99.97 at. % or 99.996 wt. %. The resistance ratio ($\rho_{300}/\rho_{4.2}$) of the heat-capacity sample was ≥ 100, which is the highest value observed for an erbium sample. Although this resistance ratio may not seem particularly large, the resistivity at 4 K still has an appreciable magnetic contribution to the total resistivity, because of the low Curie temperature (~ 19 K).

The low-temperature zero-field (1.5–80 K) and magnetic-field (1.5–20 K) heat capacities were measured using an adiabatic heat-pulse-type calorimeter.[20] We estimate the heat capacities are accurate to ±1% below 20 K, between ±2 and ±5 % between 20 and 60 K, and between ±5 and ±10 % above 60 K, with the accuracy decreasing with increasing temperature in both the 20–60 K and >60 K temperature ranges. The reproducibility from one run to another, however, is much better, except near the maximum of a large sharp heat-capacity peak: ≤1% below 40 K, 2% between 40 and 50 K, 3% between 50 and 60 K, and 4–5 % above 60 K.

Because the magnetic heat capacity could have a crystallographic dependency we checked the sample for preferred orientation, using a SCINTAG x-ray powder diffractometer. A thin slice of erbium sample was cut perpendicular to the axis of a cylinder (rod), and a full profile diffraction pattern using Cu K_α graphite monochromated radiation over the 2θ range of 20–120° was recorded. It is well known, that preferred orientation affects the intensities: particularly significant increases in the relative intensities of the diffraction planes oriented perpendicular to texture axis, and decreases in the relative intensities of the planes parallel to texture axis. We have evaluated the integrated intensities from our full profile data and compared them with the calculated ones (assuming that no preferred orientation is present in the powdered sample). Such a comparison revealed that the differences between the observed and calculated intensities never exceeded 5–7 % for all of the reflections from different diffraction zones, which is a reasonable discrepancy, typical for routine x-ray powder diffraction-structure analysis. Therefore, we conclude that our sample is free from preferred grain orientation effects within the accuracy of the method used.

III. RESULTS AND DISCUSSIONS

A. Zero field heat capacity

The measured heat capacity vs temperature of the high-purity polycrystalline erbium is shown in Fig. 1 from 1.5 to 5 K together with the results reported earlier by Dreyfus *et al.*,[2] Parks[3] and Hill, Cosier, and Hukin[6] in the form of curves calculated from C vs T equations reported by the authors[2,3,6] for the temperature regions shown. The results of Satya and Wei[4] (1.3–4.2 K), whose Er was only 92.7 at. % pure, lie between those of Dreyfus *et al.* and Parks, while those of Schmitzer *et al.*[7] (1.7–5 K) essentially fall on the solid line curve of Hill, Cosier, and Hukin. It is obvious, that our results are much closer to those reported by Hill, Cosier, and Hukin[6] and Schmitzer *et al.*[7] than those of the other studies.[2–4] The lowest temperature for which data are reported by Zimm *et al.*[8] is ~6 K and that of Skochdopole, Griffel, and Spedding[1] is 15 K.

A detailed analysis of the low-temperature (0.5 to 6.5 K) part of erbium heat capacity carried out by Hill, Cosier, and Hukin[6] includes the ^{167}Er hyperfine contribution expressed in the form $C_{\text{hf}}=aT^{-2}+bT^{-3}+cT^{-4}$, the electronic and lattice terms $C_e=\gamma T$ and $C_l=\beta T^3$, respectively, and the magnetic contribution represented as $C_m=dT^3\exp(-\Delta/T)$, or $C_m=dT^n$. Here T represents the temperature, and a, b, c, γ, β, d, Δ, and n the fit parameters. The parameters (a, b, and c) for the hyperfine contribution were fixed by using the well-established NMR results, and so was the lattice contribution parameter (β) by using the Debye temperature ($\theta_D=192$ K) determined from ultrasonic measurements. Thus the only variables were γ and one set of the two parameters

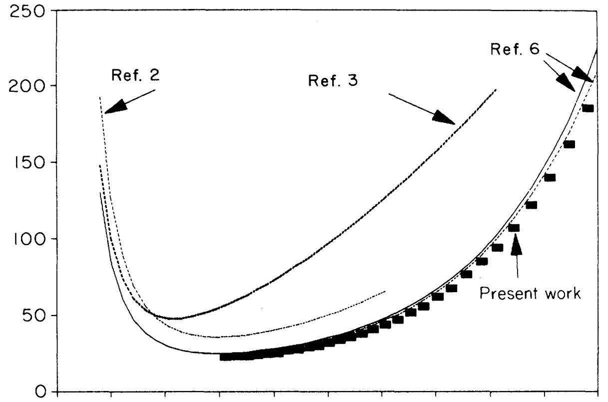

FIG. 1. The low-temperature (1.5–5 K) part of the zero-field heat capacity of erbium. The early measurements of different authors [Dreyfus *et al.* (Ref. 2), Parks (Ref. 3), and Hill, Cosier, and Hukin (Ref. 6)] are also shown. The dashed line is the fit of the data of Hill, Cosier, and Hukin to their Eq. (2) in which $C_M=dT^3\exp(-\Delta/T)$, while the solid line is the fit of their Eq. (3) in which $C_M=dT^n$.

for C_m depending upon the temperature dependence chosen. The fit using $C_m = dT^3 \exp(-\Delta/T)$ reproduced the experimental data from 0.5 to 6 K to better than 1%, while the fit that used $C_m = dT^n$ reproduced the measured data from 0.5 to 5 K to better than 2%.

A close examination of the data shown in Fig. 1 indicates that our results are consistently lower than the Hill, Cosier, and Hukin[6] data (either the solid or dashed curves). We shall concentrate on the dashed curve, since it fits their data better and is closer to our results. The temperature dependence of the heat capacity for the dashed curve was given by Hill, Cosier, and Hukin[6] as

$$C = 19.45T^{-2} + 0.585T^{-3} - 0.120T^{-4} + 10T + 0.275T^3 + 9.3T^3 \exp(-11.2/T) . \tag{1}$$

The difference in the two heat capacities,

$$\mathrm{Diff} = C_{\text{this work}} - C_{\text{Hill Eq. (1)}} , \tag{2}$$

was found to average 7%, with a maximum deviation of 12%, and to increase linearly with temperature. This suggested that the major difference between the two heat capacities was a difference in the electronic contribution. A least-squares fit of this difference leads to the result that electronic specific-heat constant γ should be reduced by 1.6 ± 0.1 mJ/mol K^2. The precision of the fit of our data to Eq. (1), with the coefficient to the electronic contribution changed from 10 to 8.4 averaged 1.5%, with a maximum deviation of 2.8%. The accuracy of our fit is comparable with that obtained by Hill, Cosier, and Hukin. The difference in electronic specific heat reported in the present paper by Hill, Cosier, and Hukin is not surprising, since none of the contributions to total heat capacity (i.e., hyperfine, lattice, and magnetic terms), except the electronic heat capacity, exhibit a strong dependence on *small amounts* of impurities, but the last is sensitive to most impurities, especially the interstitial impurities hydrogen [in Lu (Refs. 21 and 22) and in Dy (Ref. 23)] and oxygen [in Gd (Ref. 24)].

The difference in the heat capacities between the results of Hill, Cosier, and Hukin and our results could also be, in part, due to the choice of Debye temperature used to fix the coefficient β to the T^3 lattice parameters. At the time, their choice $\theta_D = 192$ K was reasonable, but subsequently several papers have been published on the heat capacity of high-purity rare-earth metals [Sc,[22] Y,[22] Gd,[24] Tb,[25] Dy,[23] and Lu (Ref. 22)] and these results suggest this Debye temperature is too high by about 15 K. Assuming a linear interpolation between Gd and Lu, we estimate $\theta_D = 177$ K. Because of the uncertainty in the coefficient of the T^3 term and the difference in electronic term we fitted our experimental data to an equation of the form

$$C = aT^{-2} + 0.585T^{-3} - 0.120T^{-4} + \gamma T + \beta T^3 + dT^3 \exp(-\Delta/T) , \tag{3}$$

where the parameters a, γ, β, d, and Δ were fitted to the experimental results. The coefficients to the T^{-3} and T^{-4} terms were fixed as indicated in Eq. (3) and are based on the well-established NMR results as discussed by Hill, Cosier, and Hukin.[6] The coefficient to the T^{-2} term, a, was kept as a variable, because it will vary in high magnetic fields and we wanted to know how it changed in such fields. Undoubtedly the coefficient to the T^{-3} and T^{-4} terms will also change with the applied magnetic field, but, since they only contribute 0.7 and 0.1 %, respectively, at the lowest temperature of our measurements keeping these two coefficients constant will not have any significant effect on the resultant fit parameters. Because of the strong correlations between the fit parameters, and because the heat capacities at low temperature compared to those at the upper temperature limit (~ 5 K) are about ten times smaller, we tried several weighting schemes so that each data point contributes approximately the same to the least-squares fit. The one chosen was

$$w = 1/C^{1/2} ,$$

TABLE I. Least-squares fit parameters of the heat capacity of erbium at zero and high magnetic fields from ~ 1.5 to ~ 5 K. The values given in the parentheses is the standard deviation in the last digit given.

	Magnetic field				
Fit parameters	0.0 T	2.46 T	5.32 T	7.53 T	9.85 T
a (mJ K/g atom)	18.0(9)	23(2)	25(2)	31(2)	37(2)
γ (mJ/g atom K^2)	8.7(1)	9.4(4)	10.3(3)	9.8(4)	10.5(3)
β (mJ/g atom K^4)	0.351(2)	0.351	0.351	0.351	0.351
d (mJ/g atom K^4)	8.9(4)	4.4(5)	5.3(5)	3.3(6)	3.8(7)
Δ (K)	11.6(3)	7.5(6)	9.0(5)	7.5(9)	9.1(9)
ξ^2 [a]	0.0029	0.0284	0.0099	0.0255	0.0244
No. of points	29	41	39	27	29
Min dev. (%)	−1.23	−3.20	−3.13	−1.56	−5.48
Max dev. (%)	1.53	2.63	3.59	3.67	2.54
Mean dev. (%)	0.55	1.41	0.96	1.87	1.44

[a] ξ^2 is the weighted sum of the squared deviations over all observations, which may be considered a criteria of the quality of the fit.

where C is the observed heat capacity.

The results are shown in Table I. As one can see, the fit of the five least-squares parameters gives quite good results, as evident from the percent deviations presented in the bottom portion of the table, especially for the zero-field data. Furthermore, the three parameters, which are not particularly sensitive to impurities, a, d, and Δ, are quite close to values reported earlier [compared to the corresponding values in Eq. (1) with the zero-field data of Table I]. The electronic specific constant, 8.7 ± 0.1 mJ/g atom K^2, is lower than that reported by Hill, Cosier, and Hukin[6] and it is about what we expected from the displacement of our results relative to those of Hill, Cosier, and Hukin (see Fig. 1 and above discussion). The Debye temperature calculated from β in 176.9 ± 0.4 K is significantly lower than that assumed by Hill, Cosier, and Hukin, but is consistent with those of Gd and Lu, which are well established.[22,24]

Figure 2 displays the heat capacity of erbium up to 21 K. Figure 2(a) shows a smooth increase of the heat capacity with temperature and these data are in good agreement (within a few percent) with the previously reported results.[1,6–8] The most interesting and unexpected results occurred in the region shown in Fig. 2(b), which includes the antiferromagnetic to ferromagnetic transition. First of all, our heat-capacity measurements demonstrate that the temperature of the heat-capacity maximum is 18.7 K [compared to 23 K (Ref. 8), 20 K (Ref. 1) or 19.2 K (Refs. 6, 7, and 13)], and that this value is the closest to the $T_c=18$ K reported in the magnetization and neutron-diffraction studies. These results show that the higher the purity of the erbium sample the lower the magnetic transformation temperature. Second, the maximum itself is enormously large and sharp. We have measured a peak value of 169.0 J/mol K, which is almost three times higher than the one reported by Hill, Cosier, and Hukin,[6] five times higher than that of Schmitzer *et al.*,[7] eight times higher than that given by Zimm *et al.*,[8] and almost nine times higher than that reported by Skochdopole, Griffel, and Spedding.[1] Figure 2(b) represents results of three of the seven independent measurements of the same sample, which were necessary because of the extremely slow thermal relaxation (this specific feature of erbium has also been mentioned by Hill, Cosier, and Hukin[6]) and the sharpness of the peak. The three runs presented in Fig. 2(b) are indicated as empty squares. Because of the extreme sharpness of the peak it is impossible to obtain points that clearly define the shape of the peak in one run using the heat-pulse technique used in this study; i.e., the temperature rise of the average pulse is about 2 or 3 times the width of the peak (0.07 K full width at half maximum). So we made seven independent runs over various temperature spans, all of which included data between 16 and 21 K, to define the peak shape and height. The results are shown in Fig. 2(c) for all the data points obtained between 18.4 and 19.2 K. One can see that agreement between different runs is quite good.

Since the existence of a thermal hysteresis effect (the peak due to ferromagnetic ordering is observed only after the sample has been cooled below 18 K) had been reported earlier,[1,6] we tried to repeat this procedure. Figure 2(b) (filled triangles) illustrates that thermal hysteresis phenomenon does occur, and there is absolutely no evidence of the giant 18.7 K peak after the sample was cooled down only to 18 K. However, any time the sam-

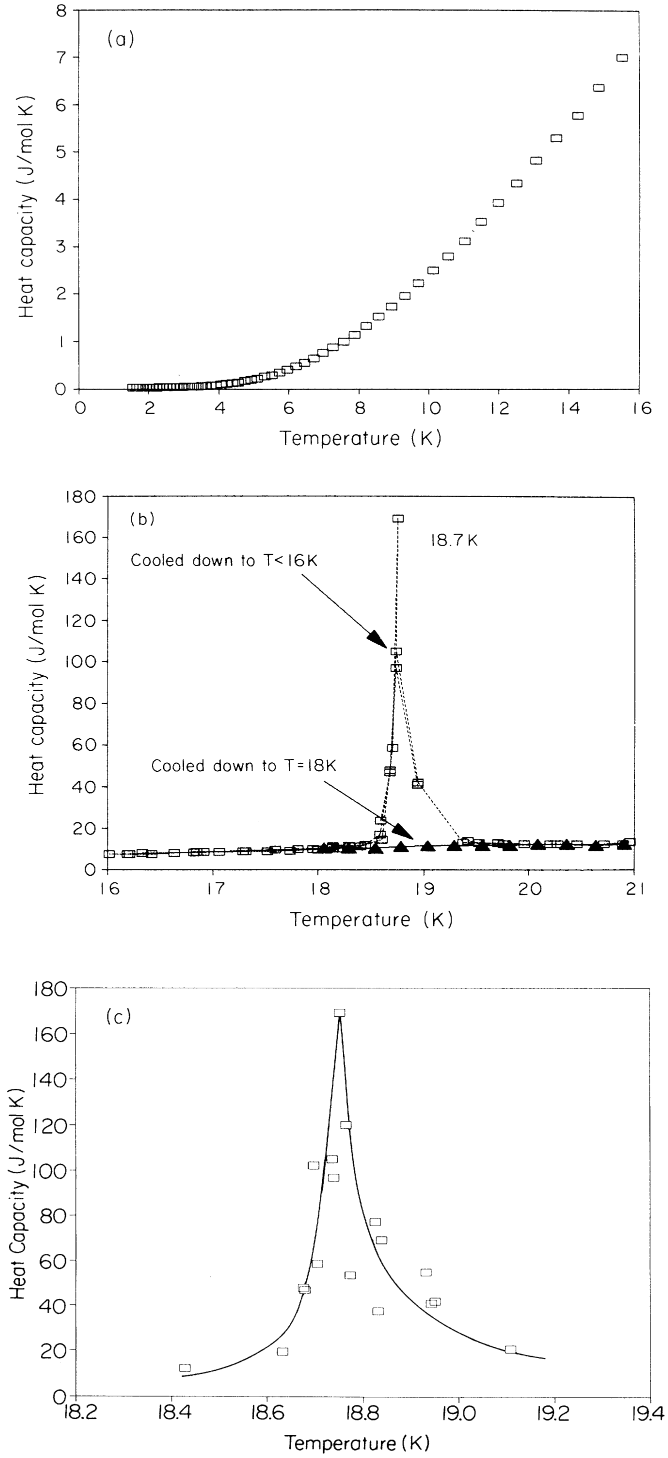

FIG. 2. The heat capacity of erbium in a region 1.5–16 K (a), 16–21 K (b), and 18.4–19.1 K (c). Lines drawn through the data points are guides for the eye.

ple was cooled below 16 K and then warmed, the transition was again observed at 18.7 K. Furthermore, we investigated the question of what would happen if the sample were to be kept at a low temperature for a long time before heat-capacity measurements were made. Measurement initiated after the sample had been cooled down to 4.2 K and kept at this temperature for 16 h showed no difference between these data and the previous results. Therefore, the conclusion that only the minimum temperature reached during the cooling, and not the time spent at the minimum, influences the erbium heat-capacity behavior, seems to be quite reasonable.

The relatively high-temperature part of the erbium heat capacity (from 20 to 80 K) is shown Fig. 3(a) and in detail from 21 to 41 K in Fig. 3(b). An obvious maximum located at $T=51.4$ K is evidence of the antiferromagnetic phase transition due to the basal plane moment ordering (usually reported $T_{N_1}=52$ K in the literature). Two more maxima are clearly visible at lower temperatures: 25.1 and 27.5 K.

Originally we thought that there was only one peak at 51.4 K and that the one low data point at ~50 K was a bad one [Fig. 3(a)]. But in view of the other experimental data (x-ray scattering, ac susceptibility, electrical resistivity, and scanning calorimetry),[12-17] which show a second transition 1–2 K below T_{N_1} we now believe that this point is a valid and reliable data point, and that we are observing a spin-slip transition occurring (at 48.9 K) just below T_{N_1}. The magnetic wave vector (τ_m) associated with this transition is $\frac{2}{7}$ and is represented in the spin-slip notation of Gibbs *et al.*[12] as ●1 (where the dot [●] represents a triplet of ferromagnetic layers that have a moment perpendicular to the plane, and the integer represents the number of quartets, four adjacent basal plane layers with identically aligned spins, which are parallel or antiparallel to the *c* axis).

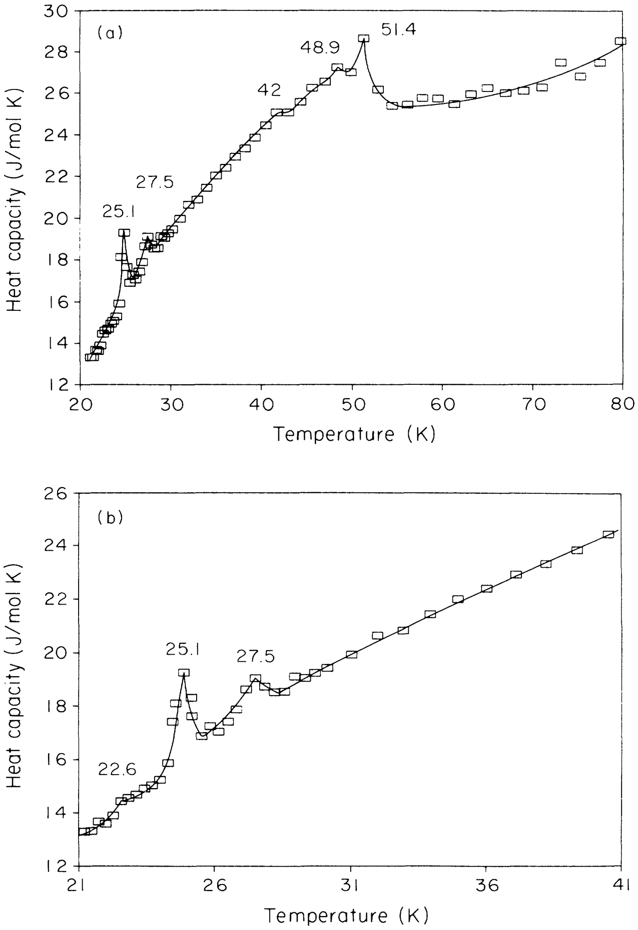

FIG. 3. The heat capacity of erbium in a region 20–80 K (a) and 21–41 K (b). The lines drawn through the data points are guides for the eye.

Similarly the flat step (the two points with identical heat capacities) at 42 K [Fig. 3(a)] is also evidence of the spin-slip transition reported by others[12-17] at 40–41 K. For this transition $\tau_m=\frac{3}{11}$ and the spin-slip structure is ●2●2.

We now turn our attention to Fig. 3(b), which shows the 27.5 and 25.1 K peaks in more detail. These two transitions are also due to spin-slip transformations: $\tau_m=\frac{5}{19}$ (●4●4) and $\tau_m=\frac{6}{23}$ (●5), respectively.

There are two other spin-slip transformations[12-17] that occur at ~34 K, $\tau_m=\frac{4}{15}$ (●3) and 20–24 K, $\tau_m=\frac{1}{4}$ (2), which we do not see in our heat-capacity measurements, although there appears to be a slight cusp at 22.6 K, which might be evidence for the latter.

The entropies of transformation for the various magnetic transitions were obtained by fitting the heat capacity to a power-series polynomial around the peaks to obtain the base line. The heat capacity, excluding the peaks, between 21 and 30 K is given by

$$C/T=0.1873+0.03242T-5.700\times10^{-4}T^2\ , \tag{4}$$

and between 30 and 60 K by

$$C/T=0.1953+0.03769T-9.416\times10^{-4}T^2 +6.309\times10^{-6}T^3\ . \tag{5}$$

The quality of the base line fits are quite good, judging by the ξ^2 values (see Table I), which are 0.0002 and 0.0001, respectively, for Eqs. (4) and (5). The entropies are calculated from the experimental data by subtracting off the base line heat capacities [Eq. (4) or (5)] using a numerical integration procedure. The results are presented in Table II. Unfortunately the precision of such an integration is not too accurate, but we believe the results are accurate in the second place after the decimal point. Because of the lack of points for the 48.9 and 51.4 peaks it is quite difficult to separate out the entropy of the individual peaks. However, Åström and Benediktsson[13] in their differential scanning calorimetry (DSC) study of erbium found that the area of the upper peak is twice as large as that of the lower peak and so we have prorated the total entropy of 0.255 J/mol K accordingly and the results are listed in Table II.

For the Curie temperature peak the base line is easily established, because when the sample is cooled down to

TABLE II. Entropies and heats of transformation for the various magnetic transformations.

Transformation identification (τ_m)	Spin-slip transition	Temp. (K)	ΔS_{tr} (J/mol K)	ΔH_{tr} (J/mol)
$T_{N_\perp}$		51.4	0.170[a]	8.7
$\frac{2}{7}$	●1	48.9	0.085[a]	4.2
$\frac{3}{11}$	●2●2	42	0.052	2.2
$\frac{4}{15}$	●3	33–35[b]		
$\frac{5}{19}$	●4●4	27.5	0.056	1.5
$\frac{6}{23}$	●5	25.1	0.116	2.9
$\frac{1}{4}$	2	20–24[b]		
T_c		18.7	1.874	35.0

[a] The total entropy was divided 2:1 for the two peaks, see text for further details.

[b] Values reported in the literature by various investigators (Refs. 12–17).

18 K the sample does not order ferromagnetically, and thus the measured heat capacity for this run is the base line [see Fig. 2(b)]. The entropy is obtained by a numerical integration procedure using the two different heat-capacity runs. This result is also given in Table II.

A comparison of the various calorimetric measurements for the Curie temperature peak is presented in Table III. The Curie temperature and the width of the peak both decrease and the peak height increases with increasing purity of the erbium sample, which is consistent with similar observations on other rare-earth metals. There is a significant increase in the magnetic entropy from the mid-1950's measurements of Skochdopole, Griffel, and Spedding[1] with the more recent results reported by Hill, Cosier, and Hukin,[6] Schmitzer *et al.*,[7] and in this study, with the exception of the sample of Zimm *et al.*,[8] which seems to have a purity comparable to that of Skochdopole, Griffel, and Spedding. The DSC measurement yielded a significantly lower magnetic entropy, but this is due to the slow thermal relaxation noted by Hill, Cosier, and Hukin[6] and also in our study. For the other peaks the thermal energy reported by Åström and Benediktsson[13] in the DSC study is generally about five times smaller than the values listed in Table II, except for the 27.5 K spin-slip transition where the energies are nearly the same.

TABLE III. The Curie temperature, breadth of the ordering temperature (full width at half maximum), and entropy of transformation from various calorimetric studies.

Curie temp. (K)	ΔT_c (K)	ΔS_{tr} (J/mol K)	Method	Reference
19.9	2.1	1.1	Adiabatic[a]	1
19.1	0.45	1.9	Adiabatic[a]	6
19.2	1.1	1.58	Adiabatic[a]	7
23	3.7	1.2	Adiabatic[a]	8
19.2	0.25	0.96	DSC[b]	13
18.7	0.07	1.874	Adiabatic[a]	This study

[a] Adiabatic heat-pulse calorimetry.

[b] High-resolution scanning microcalorimeter.

B. Magnetic-field heat capacity

Since the magnetic-field dependence of the heat capacity of Er has not been measured previously, we collected heat-capacity data on the erbium sample in the presence of a magnetic field. Figure 4(a) illustrates the low-temperature part (below $T=4$ K), Fig. 4(b) the intermediate range between 4 and 11 K, and Fig. 4(c) from 11 to 21 K (the region where the ferromagnetic cone changes an APD cone, see the introduction). The upper temperature of 21 K is the temperature limit of our apparatus for magnetic heat-capacity measurements. Before we start to describe these results we should mention that during the measuring process we observed extremely strong magnetocaloric effects. The measurements were taken according to the following procedure: For each run the sample was cooled down at zero field to the lowest possible temperature (~ 1.5 K) and then an appropriate magnetic field was applied by increasing the field at a rate of about $0.1T$ per min). During the process of applying the field, the sample was kept in thermal contact with helium pot ($T \sim 1.5$ K), and even under these conditions we detected temperature rises of up to 10–12 K. The heat-capacity measurements at each field were started after the sample had cooled down to 1.5 K.

As seen in Fig. 4(a) the applied magnetic field increases the low-temperature tail, which appears to be due to the hyperfine contribution to the heat capacity. In order to see if this is correct and to obtain more quantitative information, the heat capacity runs at the four nonzero magnetic fields were fitted to Eq. (3), except for keeping the β term constant at the zero-field value, as well as the coefficients to the T^{-3} and T^{-4} terms, as discussed earlier. The results are tabulated in Table I and are plotted in Fig. 5. The magnetic-field dependence of the hyperfine field coupling constant is shown in Fig. 5(a), where it is seen that it nearly doubles when the field is increased from zero to 10 T. This increase indicates that the hyperfine coupling between the nucleus and the unpaired valence electrons at the nucleus is positive, which is consistent with theory and electron-spin-resonance measurements.[26] The effective magnetic field at the nucleus, H_{eff}, can be calculated from the coefficient of the T^{-2} term, a, and it is found to be 7.2 ± 0.2 MOe at zero field, exactly the same value reported by Krusius, Pickett, and Veuro.[5] With increasing applied magnetic field, H_{eff} also increases to 8.1 at 2.46 T, 8.4 at 5.32 T, 9.4 at 7.53 T, and 10.3 MOe at 9.85 T.

The field dependence of the other parameters (electronic specific constant, γ, the coefficient to the magnetic heat contribution, d, and the energy gap, Δ) are shown in Fig. 5(b). All three parameters change with increasing magnetic field, but seem to remain constant for $H \geq 2.5$ T. However, for the electronic specific-heat constant, one could probably draw a straight line with a constant slope from $H=0$ to $H=9.85$ T and it would fit the data just as well as the curve with step in it at ~ 2 T, as shown in Fig. 5(b). The steps in the d vs H and Δ vs H data is more apparent and thus easily justified. The logic for drawing steps at $H=2$ T in the three curves is the fact that at 4.2 K the distorted spiral component of the magnetic moments in the basal plane of erbium abruptly changes into an inclined fan-type structure.[27] Such a sharp step is also seen at $H=2$ T in the magnetic moment when the applied magnetic field is parallel to either the a or b axis of erbium.[27] Thus the steps in d and Δ are not unexpected in view of the magnetic behavior.

The step in the electronic specific constant suggests that the density of states at the Fermi level increases by 15% when this change in the magnetic structure occurs

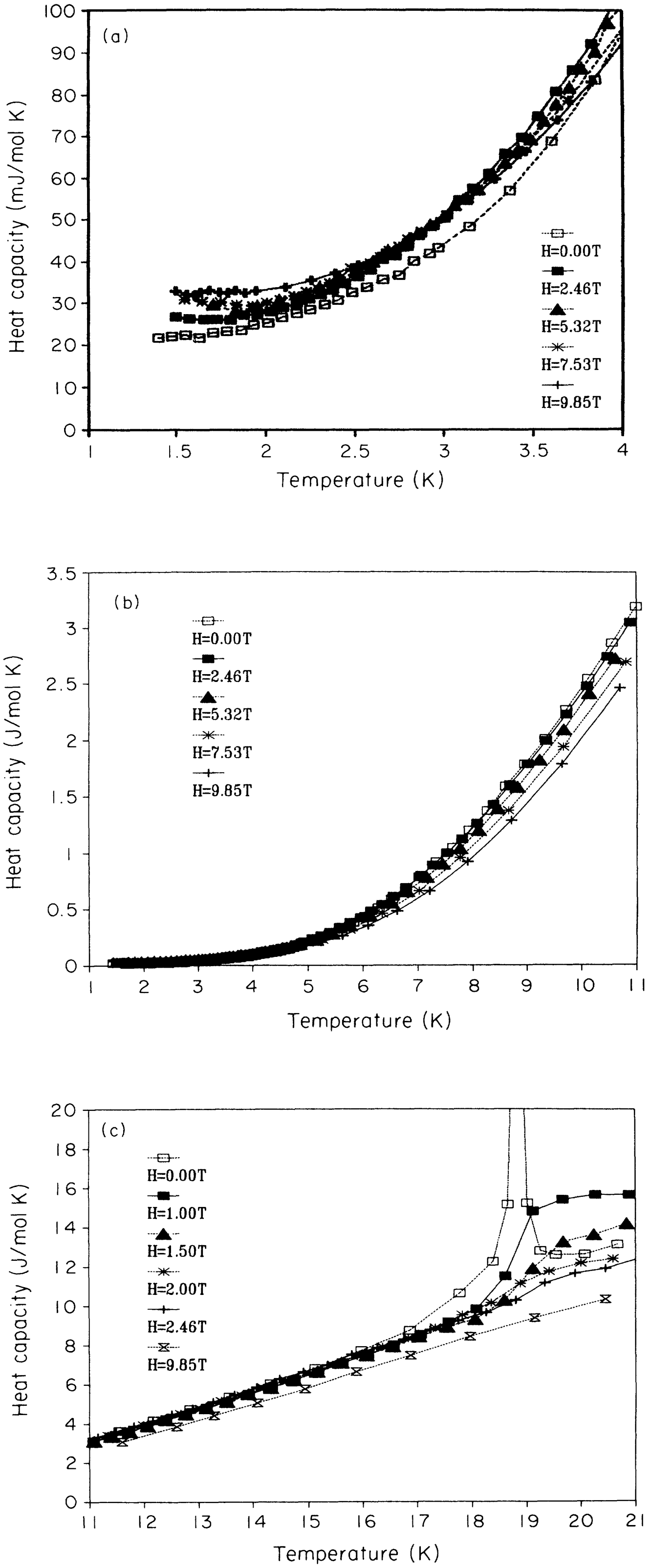

FIG. 4. The magnetic heat capacity of erbium in a region 1.5–4 (a), 1.5–11 K (b), and 11–21 K (c). Lines drawn through the data points are guides for the eye.

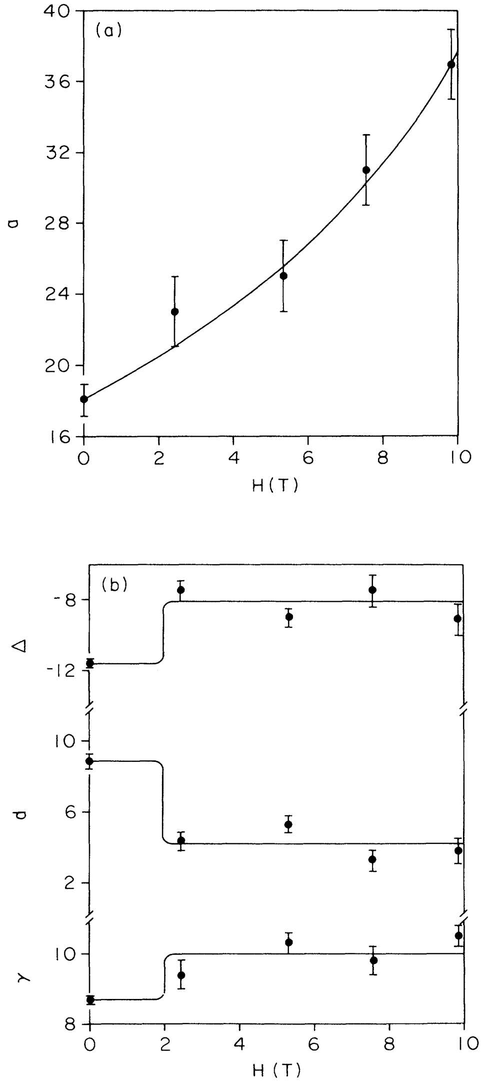

FIG. 5. The magnetic-field dependence of the fit parameters [to Eq. (3)]: the hyperfine constant a (a); the electronic specific constant γ, the coefficient d to the magnetic heat contribution term, and the energy gap Δ in the exponential part of the magnetic heat-capacity term (b). The unusual step at $H\sim 2$ T in the plots for γ, d, and Δ is discussed in the text. The value of the horizontal lines for each parameter for $H\geq 2.5$ T is the average value of the four data points.

at $H=2$ T. As far as we are aware this is the first time anyone has observed a sudden change in the density of states at the Fermi level in a rare-earth material using heat-capacity measurements. This increase in γ is reasonable in view of the fact that spin rearrangement modifies the spiral structure wave vector so that some of the superzone gaps are destroyed and the density of states at the Fermi level is increased. As noted above one could fit the data just as well by a linear line with a positive slope, which would suggest a continuously increasing density of states with increasing field. This would, however, be difficult to explain, since theory[28,29] suggests that high magnetic fields would partially quench the spin-wave enhancement of ferromagnetic erbium (or any other heavy lanthanide ferromagnet) and thus *lower* the electronic specific-heat constant by 4% or less at 10 T. Thus a constant γ value, both below and above the step, would be consistent with our current knowledge of the electronic density of states in metals.

We will now turn our attention to the influence of magnetic fields on the behavior of erbium at higher temperatures. As one can see, at $T\sim5$ K the high magnetic field significantly reduces the total heat capacity of pure erbium and this reduction does not level off even at highest field available (9.85 T), see Fig. 4(b). This behavior is typical of a ferromagnet in which the entropy is shifted from below the Curie temperature to well above it. Unfortunately our upper temperature limit is 21 K in the high-field apparatus, but the beginning of such a shift above the Curie temperature is quite evident [Fig. 4(c)].

Near the ordering temperature, even low magnetic fields drastically affect the heat capacity. The sharp peak at 18.7 K for $H=0$ T shifts towards higher temperatures, becomes remarkably broader, and decreases in magnitude (as much as ten times smaller) when the external magnetic field is 1 T. A further increase of the field continues to affect this maximum similarly, and finally at $H=2.46$ T the 18.7 K peak is hardly evident [Fig. 4(c)]. As the 9.85 T data show, there is no sign of the ferromagnetic ordering peak.

IV. CONCLUSION

Zero-field and high-magnetic-field (up to $H=9.85$ T) low-temperature heat-capacity measurements of high-purity polycrystalline erbium have shown that the electronic specific-heat coefficient, reported earlier to be 10 mJ/mol K^2, is significantly lower and has a value of 8.7 ± 0.1 mJ/mol K^2, but abruptly increases to 10.0 ± 0.5 mJ/mol K^2 at $H\sim2$ T due to a spin reorientation in the basal plane. The difference in the zero-field values is due to the fact that we have a higher purity sample. The Debye temperature is found to be 176.9 ± 0.4 K, which is consistent with Debye temperatures of Gd, Tb, and Lu. The zero-field heat-capacity maximum due to ferromagnetic ordering (at 18.7 K) has enormously large amplitude—169 J/mol K (which is the highest ever observed)—and exceeds an earlier measured peak height by a factor of nearly 3. Other zero-field heat-capacity anomalies include a maximum at 51.4 K (antiferromagnetic ordering in the basal plane), two quite distinct maxima at 27.5 and 25.1 K, a less distinct peak at 48.9 K, and a flat step at 42 K. The last four anomalies are associated with spin-slip transitions between different commensurate antiferromagnetic structures.

The high-magnetic-field studies established that the magnetic field shifts the ferromagnetic phase transition towards higher temperatures, which was expected, and therefore decreases the total erbium heat capacity just below the transition temperature and down to about 5 K. At lower temperatures ($T<4$ K) a notable increase in the heat capacity compared to zero-field results was detected and is caused by the positive hyperfine coupling in ^{167}Er and an increase in the electronic density of states at the Fermi level.

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