Magnetic ordering and spin reorientation in $ErGa_3$

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Calorimetric measurements between 0.3 and 10 K have been made on a single crystal of the $AuCu_3$-type cubic compound $ErGa_3$. The temperature dependence of specific heat exhibits an antiferromagnetic ordering-induced peak near 2.7 K, a second peak at 2.5 K due to spin reorientation, and a Schottky anomaly with crystal-field parameters $x=0.17$ and $W=0.22$ K, all in agreement with the results from neutron studies. The sum of the calculated entropies associated with the order-disorder process ($R\ln 2$) and the crystal-field effect, respectively, is lower by $0.1R$ than the experimentally derived magnetic entropy values at approximately 6–10 K. This difference provides an estimate of a 2-J/mol latent heat for the spin rotation process. An anticipated transition from an amplitude-modulated magnetic structure to an equal magnetic-moment structure at temperatures near $T_N/2$ was not observed.

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Rare-earth-based compounds often undergo magnetic ordering, some of them followed by spin reorientation at lower temperatures. Among the different experimental techniques, calorimetric measurements play a unique role in providing thermodynamic quantities including energy and entropy associated with these processes. In a recent paper[1] on Er_3Ge_4, a specific-heat peak at 7 K and a second one at 3.5 K confirmed the antiferromagnetic ordering and a spin reorientation, respectively, suggested by neutron diffraction. A sizable latent heat was obtained for the second transition. This report describes a similar work from 10 down to 0.3 K on another Er-intermetallic $ErGa_3$. An antiferromagnetic transition in this compound was first identified by Morin *et al.*[2] More extensive dc magnetization and neutron-diffraction studies by Murasik *et al.*[3,4] indicated that the ordering at the Néel temperature $T_N=2.83$ K occurred through a continuous transition and the magnetic structure appeared to be an incommensurate sinusoidally modulated one. Furthermore, they revealed two successive spin reorientations in zero applied field at $T_1=2.6$ K and T_2 in the vicinity of T_N, respectively. With lowering temperature one may expect the amplitude-modulated structure to evolve or transit toward an equal moment structure, of an antiphase type if it remains incommensurate or simple commensurate.

$ErGa_3$ single crystals were grown by the molten-metal solution method. The melt of composition of 90-at. % Ga ($6N$) and 10-at. % Er ($3N$) was slowly cooled from 920 °C to 350 °C at the rate of 0.8 °C/h before a rapid cooling to avoid the formation of $ErGa_6$ in a peritectic reaction. This procedure yielded single crystals of stoichiometric $ErGa_3$ immersed in an excess of pure gallium, which was easily removed. The high quality of the crystals was confirmed by x-ray diffraction showing the expected cubic $AuCu_3$-type structure. Complemented by ac susceptometry, calorimetric measurements were made using a thermal-relaxation approach. A milligram-size specimen was thermally anchored with a minute amount of grease to a sapphire holder, which had a Cernox temperature sensor and a nickel-chromium alloy film as the Joule-heating element. The holder was linked thermally to a copper block by four Au-Cu alloy wires. The temperature of the block could be raised in steps but held constant when a heat pulse was applied to the specimen. Following each heat pulse, the specimen temperature relaxation rate was monitored to yield a time constant τ. Heat capacity was then calculated from the expression $c=\kappa\tau$, where κ is the thermal conductance of the Au-Cu wires. The heat capacity of the specimen holder was measured separately for addenda correction. The specific heat of the specimen was then obtained from $C=(c-c_{\text{addenda}})/(m/M)$ with m and M being the specimen mass and the molar mass of $ErGa_3$ (376.42 g/mol), respectively.

Figure 1 presents the temperature dependence of the specific heat of $ErGa_3$. Also shown are the data for an isostructural but nonmagnetic reference compound $LuGa_3$, which were obtained using a quasiadiabatic heat-pulse technique in Wroclaw. There are two maxima for $ErGa_3$, more clearly in the inset, at 2.5 and 2.7 K, respectively. The higher-temperature peak is believed to be associated with the antiferromagnetic ordering, even though 2.7 K is lower than the Néel temperature $T_N=2.83$ K as determined from magnetic-susceptibility measurements.[3] Such a phenomenon may be expected in systems with incommensurate amplitude-modulated magnetic structures when contribution of higher harmonics to the order parameter is large enough.[5] The peak at 2.5 K undoubtedly corresponds to the afore-mentioned T_1, arising from an abrupt reorientation of Er^{3+} spins from nearly the $\langle 110\rangle$ direction towards the $\langle 100\rangle$ axis.[3] However, judging from the calorimetric data below 2.5–0.3 K, there is

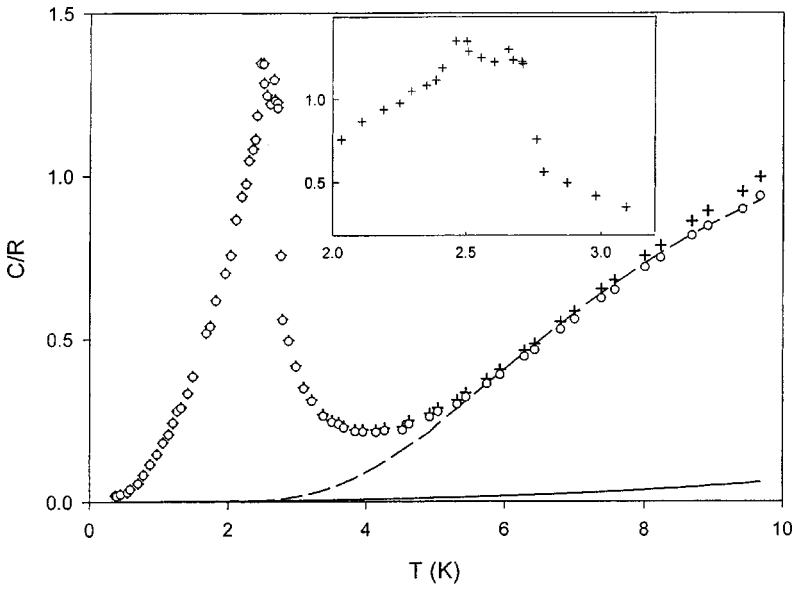

FIG. 1. Temperature dependence of specific heat of $ErGa_3$ (+) and the nonmagnetic reference compound $LuGa_3$ (solid curve). Also shown for $ErGa_3$ are the magnetic contribution (○), $C(m) = C - C(LuGa_3)$, and the calculated Schottky contribution (dashed curve) for comparison. Inset: Expanded plot revealing two peaks at 2.5 and 2.7 K, respectively.

no observable anomaly near $T_N/2$. It indicates that the squaring of the amplitude-modulated magnetic structure of $ErGa_3$ goes through an evolution of higher-order harmonics of the order parameter.[6]

The magnitude of the spin rotation effect in Fig. 1 is relatively small as compared to that in Er_3Ge_4.[1] It is understandable, realizing that the complex magnetic behavior of orthorhombic Er_3Ge_4 arises from the intrinsic magnetic frustration caused by two nonequivalent Er^{3+} sites. In contrast, cubic $ErGa_3$ has a much higher structural symmetry, and the transition at T_1 involves only a relatively minor moment tilting. It is not surprised then that the other transition at T_2 near T_N has no distinguishable effect on specific heat.

In analyzing the calorimetric data, the total specific heat needs first to be delineated into its lattice, electronic, and magnetic contributions:

$$C = C(l) + C(e) + C(m). \tag{1}$$

This is done by assuming that the lattice plus electronic contributions are equal to the specific heat of nonmagnetic $LuGa_3$ ($\gamma = 6.7$, $\beta = 0.47$ mJ/mol K^4 with a corresponding $\theta_D = 161$ K). The magnetic contribution $C(m) = C - C(LuGa_3)$ is then calculated and shown as a function of temperature in Fig. 1. It actually contains three components:

$$C(m) = C_{\text{O-D}} + C_{\text{sr}} + C_{\text{Sch}}. \tag{2}$$

$C_{\text{O-D}}$ and C_{sr} are associated with the order-disorder (O-D) process and the spin rotation, respectively, whereas C_{Sch} is a Schottky term originating from the crystal-field (CF) splitting of the $^4I_{15/2}$ multiplet of Er^{3+} ions. $C_{\text{O-D}}$ and C_{sr} dominate $C(m)$ below T_N. The short-range-ordering contribution persists to almost 6 K. In general, one does not have an easy handle on critical phenomena, but the paramagnetic behavior of C_{Sch} can be determined from

$$C_{\text{Sch}}/R = (\langle E^2 \rangle - \langle E \rangle^2)/k_B^2 T^2, \tag{3}$$

where R and k_B are the gas constant and Boltzmann's constant, respectively, and a statistical average over the CF levels with energy E_i is defined as

$$\langle x \rangle = \frac{\sum_{i=1}^{n} x_i \exp(-E_i/k_B T)}{\sum_{i=1}^{n} \exp(-E_i/k_B T)}. \tag{4}$$

Accordingly, the experimental data of $C_{\text{Sch}} \cong C(m)$ between approximately 6 and 10 K are reasonably well fitted by CF parameters $x = 0.17$ and $W = 0.22$ K, following the scheme of Lea, Leask, and Wolf.[7] These parameters give a doublet Γ_7 as the ground state, a quartet $\Gamma_8^{(1)}$ at 28 K as the first-excited level, and an overall CF splitting equal to 110 K. They agree very well with parameters $x = 0.19$ and $W = 0.25$ K determined directly by inelastic neutron scattering.[4]

It is possible to obtain a reasonable estimate of the latent heat associated with the spin rotation from entropy consideration. Figure 2(a) shows a plot of $C(m)/T$ versus T, from which the magnetic entropy is derived from

$$S(m) = \int [C(m)/T] dT \tag{5}$$

and presented in Fig. 2(b). Following Eq. (2), $S(m)$ also consists of three components:

$$S(m) = S_{\text{O-D}} + S_{\text{sr}} + S_{\text{Sch}} = \int (C_{\text{O-D}}/T) dT + \int (C_{\text{sr}}/T) dT + \int (C_{\text{Sch}}/T) dT. \tag{6}$$

While the exact determination of $C_{\text{O-D}}$ and C_{sr} is difficult, one has nevertheless a maximum value of $S_{\text{O-D}} = R \ln 2$ or $S_{\text{O-D}}/R = 0.693$ for the ground-state doublet of Er^{3+} ions. At

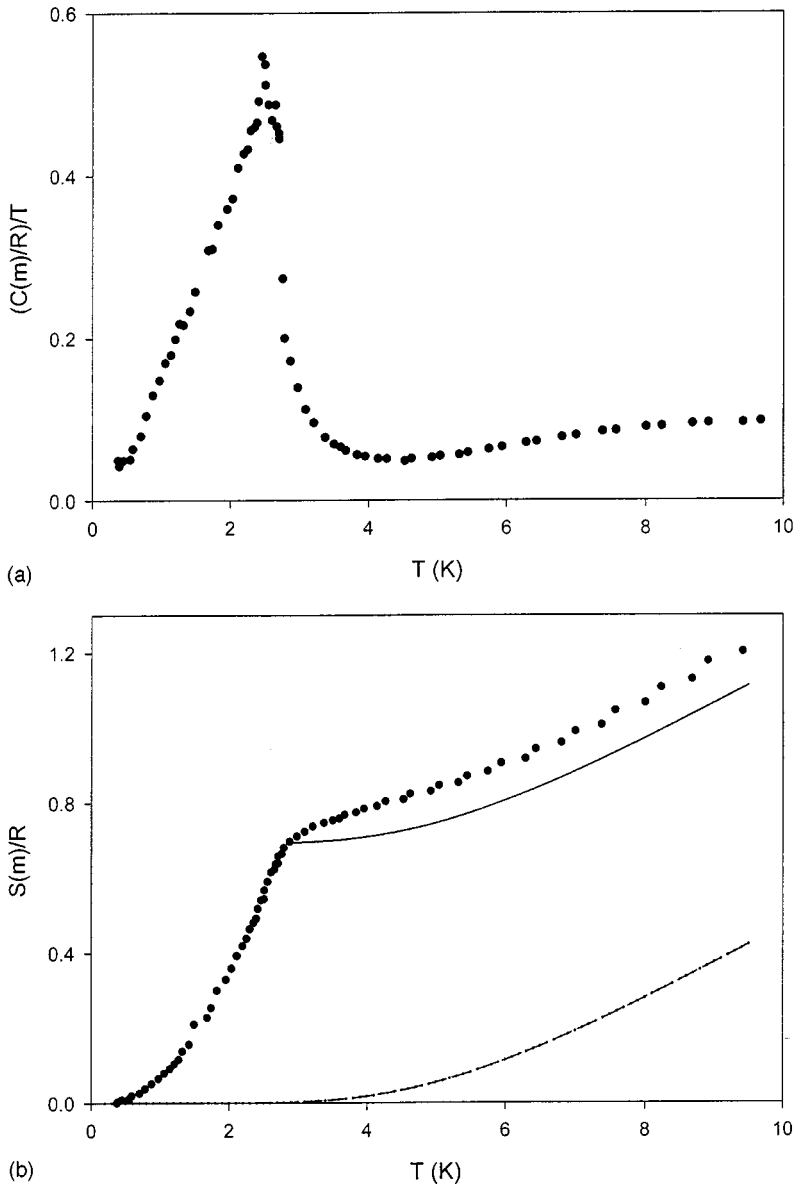

FIG. 2. (a) $C(m)/T$ versus T as basis for entropy calculations. (b) Temperature dependence of magnetic entropy. Note the S_{sr}-caused parallel difference above ~6 K between the experimental data (●) and the solid line, which represents the sum of $R \ln 2$ for $S_{O\text{-}D}$ and S_{Sch} (dashed line) associated with the CF splitting.

a first look, the experimental value of $S(m)/R$ in Fig. 2(b) is indeed close to 0.7 at T_N. However, the maximum $S_{O\text{-}D}$ value would not be achieved until all short-range ordering beyond T_N vanishes. Judging from Fig. 1, this needs to reach somewhere close to 6 K. Consequently, the seemingly coincidental observation of $S(m)/R \cong \ln 2$ at T_N gives a clear signal of the S_{sr} contribution below T_N, where S_{Sch} is negligible.

Finally, if the spin rotation were absent, the expected $S(m)$ between approximately 6 and 10 K should follow the solid line in Fig. 2(b), which represents simply the sum of $R \ln 2$ and S_{Sch} as calculated from the calorimetrically determined crystal-field parameters. Instead, the actually observed $S(m)$ values are higher by a roughly temperature independent $0.1R$, a quantity now assigned to S_{sr}. Since this spin rotation occurs near 2.5 K, $S_{sr} \cong 0.1R = 0.83$ J/mol K would lead to a small latent heat of the order of 2 J/mol. In comparison, it is 30 or 10 J/mol Er in Er_3Ge_4.

In conclusion, calorimetric data of $ErGa_3$ support the findings from magnetic and neutron studies on magnetic transitions at T_N and T_1, with additional information in terms of the associated entropy and latent heat. No indication of an additional phase transition at $T_N/2$ is observed in the presented data, contrary to the expectations. The anticipated transition near $T_N/2$ is from the amplitude-modulated magnetic structure to an equal magnetic-moment structure. Most likely, with the temperature lowering this structure evolves to an antiphase one through growing of higher-order harmonics in the order parameter.

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