Magnetic ordering and spin reorientation in ErGa₃

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Calorimetric measurements between 0.3 and 10 K have been made on a single crystal of the AuCu₃-type cubic compound ErGa₃. 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 0.1 R 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 paper1 on Er₃Ge₄, 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 ErGa₃. 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 Neél 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.

ErGa₃ 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 ErGa₆ in a peritectic reaction. This procedure yielded single crystals of stoichiometric ErGa₃ 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 AuCu₃-type structure. Complemented by ac susceptibility, 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 \( \tau \). Heat capacity was then calculated from the expression \( c = \kappa \tau \), where \( \kappa \) 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 ErGa₃ (376.42 g/mol), respectively.

Figure 1 presents the temperature dependence of the specific heat of ErGa₃. Also shown are the data for an isostructural but nonmagnetic reference compound LuGa₃, which were obtained using a quasiadiabatic heat-pulse technique in Wroclaw. There are two maxima for ErGa₃, 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 Neél 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 Er³⁺ spins from nearly the (110) direction towards the (100) axis.3 However, judging from the calorimetric data below 2.5–0.3 K, there is
Contributions are equal to the specific heat of nonmagnetic
This is done by assuming that the lattice plus electronic con-
ting of the 4I_{15/2} multiplet of Er^{3+} process and the spin rotation, respectively, whereas
ErGa_3 has a much higher structural symmetry, and the tran-
 rhombic Er_3 Ge_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 trans-
 ation 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:

\[ C = C(l) + C(e) + C(m). \] (1)

This is done by assuming that the lattice plus electronic contri-
butions are equal to the specific heat of nonmagnetic
LuGa_3 (\( \gamma = 6.7, \beta = 0.47 \text{ mJ/mol K}^4 \)) with a corre-
spending \( \theta_D = 161 \text{ K} \). The magnetic contribution \( C(m) = C - C(\text{LuGa}_3) \) is then calculated and shown as a function of
temperature in Fig. 1. It actually contains three components:

\[ C(m) = C_{O-D} + C_{sr} + C_{Sch}. \] (2)

\( C_{O-D} \) 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) split-
ting of the \(^{4}I_{15/2}\) multiplet of Er\(^{3+}\) ions. \( C_{O-D} \) and \( C_{sr} \) domi-
nate \( C(m) \) 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

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

where \( R \) and \( k_B \) are the gas constant and Boltzmann’s con-
stant, respectively, and a statistical average over the CF lev-
els with energy \( E_i \) is defined as

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

Accordingly, the experimental data of \( C_{Sch} \cong C(m) \) between
approximately 6 and 10 K are reasonably well fitted by CF
parameters \( x = 0.17 \) and \( W = 0.22 \text{ K} \), following the scheme of
Lea, Leask, and Wolf.\(^7\) These parameters give a doublet \( \Gamma_7 \)
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 \( W = 0.25 \text{ K} \) deter-
mined 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 consider-
ation. Figure 2(a) shows a plot of \( C(m)/T \) versus \( T \), from
which the magnetic entropy is derived from

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

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

\[ S(m) = S_{O-D} + S_{sr} + S_{Sch} = \int \frac{(C_{O-D}/T)dT}{T} + \int \frac{(C_{sr}/T)dT}{T} + \int \frac{(C_{Sch}/T)dT}{T}. \] (6)

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

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 (○), \( C(m) = C - C(\text{LuGa}_3) \), and the calculated Schottky
contribution (dashed curve) for comparison. Inset:
Expanded plot revealing two peaks at 2.5 and
2.7 K, respectively.
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 $S_{O-D}$ 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 $S(m)/R=\ln 2$ 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 $R \ln 2$ for $S_{O-D}$ 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 0.1$R$, a quantity now assigned to $S_{sr}$. Since this spin rotation occurs near 2.5 K, $S_{sr}=0.1R=0.83$ 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$_3$Ge$_4$.

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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