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Magnetic and calorimetric studies of antiferromagnetic transitions in erbium sesquisulfide

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Abstract

Magnetic measurements reveal an antiferromagnetic transition in erbium sesquisulfide $\text{ErS}_{1.5}$ (Er_2S_3). The Néel temperature T_N decreases from approximately 3 K at low fields to below 1.8 K at 9000 G. A Curie–Weiss fit to the low-field data between 100 and 300 K yields an effective magnetic moment of $9.65 \mu_B$ per Er^{3+} . Zero-field calorimetric measurements between 0.7 and 8 K also show a corresponding specific heat peak at T_N . Not expected, however, is the presence of a lower-temperature specific heat shoulder near 2 K. An entropy analysis indicates that both anomalies provide a total of $R \ln 2$ as expected for the Er^{3+} ordering, suggesting that the two non-equivalent Er^{3+} sites in the monoclinic lattice have different transition temperatures near 3 and 2 K, respectively.

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Rare-earth compounds often exhibit intriguing magnetic behaviors. Many undergo magnetic ordering at low temperature. Due to their complicated magnetic structures, some of the compounds show further complications below the ordering temperatures, as evidenced by magnetic measurements or direct observations made by neutron diffraction. In contrast, calorimetrically determined specific heat data have the unique advantage

in helping elucidate the nature of the anomalies through a derived entropy analysis. For example, a second specific heat peak below that at the Néel temperature $T_N = 7$ K in Er_3Ge_4 yields a sizable latent heat associated with a spin reorientation [1], while two specific heat peaks for $\text{Ce}_3\text{Al}_{11}$ [2] correspond to a ferromagnetic transition at 6.2 K and an antiferromagnetic transition at 3.2 K, respectively. On the other hand, the superconductors $\text{GdBa}_2\text{Cu}_3\text{O}_7$ [3] and $\text{GdBa}_2\text{Cu}_4\text{O}_8$ [4] show a shoulder in their temperature dependence of specific heat below $T_N = 2.2$ K, which identifies a spin quantum fluctuation in the ordered state [5].

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In an earlier calorimetric study on the rare-earth sesquisulfide series [6], $\text{ErS}_{1.5}$ (Er_2S_3) shows a tendency towards a magnetic transition near 3 K. This study extends the earlier measurements to lower temperatures to reveal the ordering process. The sesquisulfide compound was prepared by direct combination of erbium and sulfur and grown as an ingot from the melt. Chemical analysis shows a nearly stoichiometric composition of $\text{ErS}_{1.491 \pm 0.005}$. X-ray diffraction analysis of the ingot material, part of which formed the sample being used here, confirms the monoclinic structure (space group $\text{P2}_1/\text{m}$) of $\delta\text{-ErS}_{1.5}$ as reported by White et al. [7]. Along with 18 S^{2-} ions in each unit cell, there are 12 Er^{3+} ions occupying two non-equivalent sites. White et al. [7] provided a figure showing six of the Er^{3+} ions in a six-fold coordinate and the other six in a seven-fold coordinate. Zeeman splitting of the $^4\text{S}_{3/2}$ Stark levels in the absorption spectrum also confirms two non-equivalent sites in $\text{ErS}_{1.5}$ [8]. In fact, the optical Zeeman and the present magnetic and calorimetric studies were carried out on samples from the same ingot material.

Magnetic measurements were made at various applied fields H between 50 and 9000 G, using a superconducting quantum interference device. Fig. 1 presents the magnetic susceptibility at 50 G, showing an antiferromagnetic transition near 3 K. As shown in the inset, this is consistent with

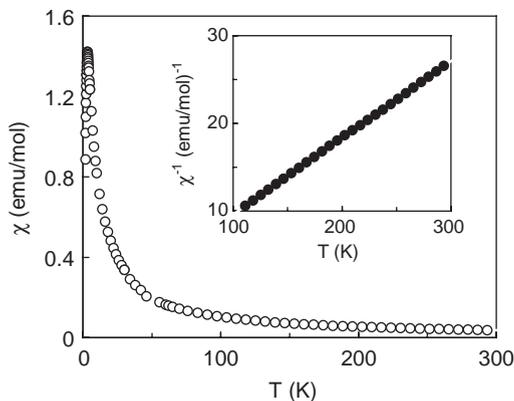


Fig. 1. Temperature dependence of magnetic susceptibility at 50 G, showing a low-temperature antiferromagnetic transition. Inset, A Curie–Weiss plot.

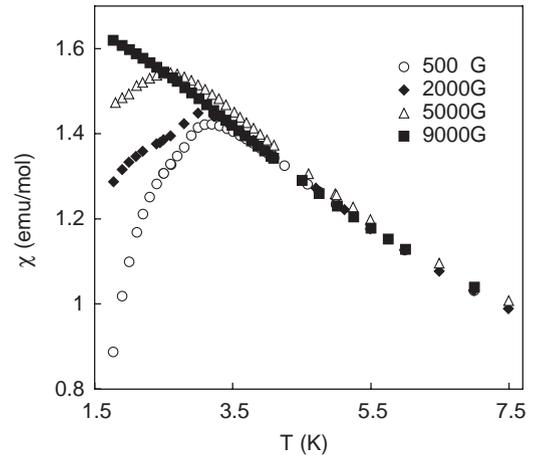


Fig. 2. Temperature dependence of magnetic susceptibility at higher fields.

a negative paramagnetic intercept, $\theta_p = -9.84$ K for a simple Curie–Weiss fit, $\chi = C^*/(T + \theta_p)$ for higher-temperature data between 100 and 300 K. An effective magnetic moment of $9.56 \mu_B$ per Er^{3+} , comparable with the value of $9.59 \mu_B$ for a free ion, is obtained from the Curie constant $C^* = 11.4$ (emu/mol) K. Further confirmation of antiferromagnetic ordering comes from the negative field effect on the ordering temperature in Fig. 2. Starting from 3 K at low fields, the transition becomes gradually suppressed to lower temperatures as the field increases, and falls below 1.8 K at 9000 G. Fig. 3 summarizes the field dependence of T_N .

Calorimetric measurements between 0.7 and 8 K were also made using a thermal-relaxation technique. An mg-size specimen was thermally anchored with a minute amount of grease to a sapphire holder. A semiconducting film and a highly resistive film were deposited onto the holder to serve as the temperature sensor and the Joule-heating element, respectively. The holder was linked thermally to a copper block by four Au–Cu alloy wires. The temperature of the block can be raised in steps, but it is held constant when a heat pulse is 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

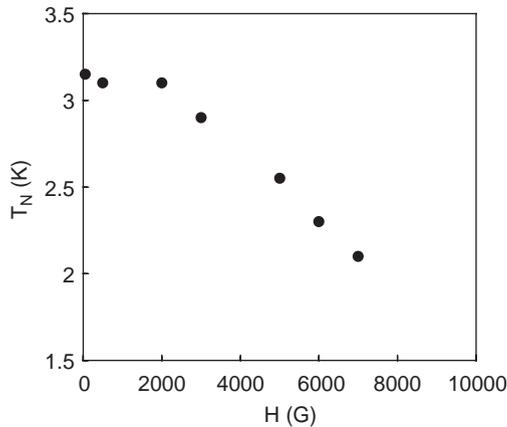


Fig. 3. Field-dependence of Néel temperature, which falls below 1.8 K at 9000 G.

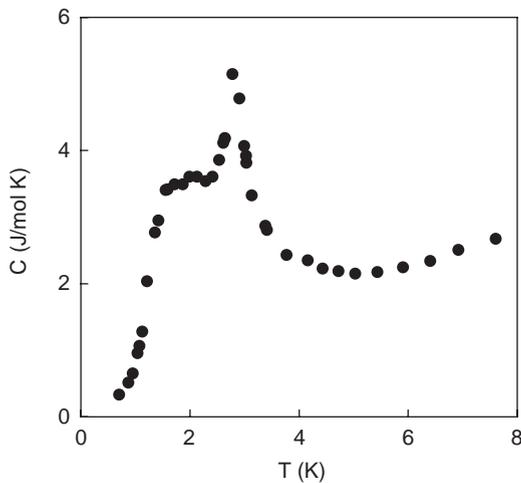


Fig. 4. Temperature dependence of specific heat, showing a peak at 2.8 K and a shoulder near 2 K.

the Au–Cu wires. The heat capacity of the specimen holder was measured separately for addenda correction. The specific heat of the specimen was obtained from $C = (c - c_{\text{addenda}}) / (m/M)$ with m and M being the specimen mass and the molar mass, respectively.

The results are shown in Fig. 4 as the temperature dependence of specific heat. The lattice contribution to specific heat can be represented approximately by that of non-magnetic $\text{LuS}_{1.5}$ [6]. At $0.258 \text{ T}^3 \text{ mJ/mol K}$ ($\theta_D = 265 \text{ K}$), it

represents only 0.7% of the total specific heat at 4 K and even less in the temperature range below. Therefore, the uncertainty introduced by the somewhat different structure of $\varepsilon\text{-LuS}_{1.5}$ is relatively insignificant. Similarly, a possible electronic term due to the minor non-stoichiometry of the specimen is also negligible, considering that the main objective of this study is the determination of the much larger magnetic effect. The specific heat behavior in Fig. 4 must be then magnetic in nature. Most pronounced is a well-defined peak at 2.8 K. In corroboration with the aforementioned magnetic data, this peak reflects the antiferromagnetic transition. As temperature increases, the specific heat exhibits a quick drop but tails off slowly above approximately 4 K. It is partly due to the persistence of short-range ordering above T_N , but also reflects the low-temperature tail of a crystal field-induced Schottky contribution [9]. Of a greater surprise is the specific heat shoulder observed below T_N that may represent an unresolved second peak near 2 K, superimposing over the lower-temperature side of the first peak. Such double peaks can be the consequence of different origins. For Er^{3+} , spin fluctuation as seen in $\text{GdBa}_2\text{Cu}_3\text{O}_7$ [3] and $\text{GdBa}_2\text{Cu}_4\text{O}_8$ [4], can be ruled out because such an effect is theoretically pronounced only in large spin systems such as Gd^{3+} with $S = 7/2$ [5]. A more likely explanation is attributed to the Er^{3+} ions occupying two non-equivalent sites in the monoclinic structure as mentioned above. The observed structure in Fig. 4 may represent two slightly different ordering temperatures for Er^{3+} in the two sites. The following entropy analysis is carried out to confirm this suggestion.

First, the specific heat data are replotted in Fig. 5 in the format of C/T versus T . A simple integration, $\Delta S = \int (C/T) dT$, yields the increasing entropy with increasing temperature in Fig. 6. For Er^{3+} ions ($J = 15/2$) with a ground-state doublet, magnetic entropy of $R \ln 2 = 5.76 \text{ J/mol K}$ is expected. Indeed, such a value is obtained at near 6 K, suggesting that both peaks are indeed associated with the magnetic ordering processes, instead of any spin reorientation as in Er_3Ge_4 [1]. Otherwise, additional entropy would prevail. Also, unlike $\text{Ce}_3\text{Al}_{11}$ [2], only antiferromagnetic-type

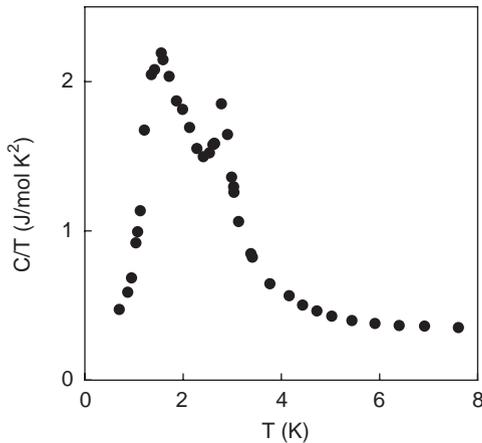


Fig. 5. Temperature dependence of C/T as a basis for entropy determination.

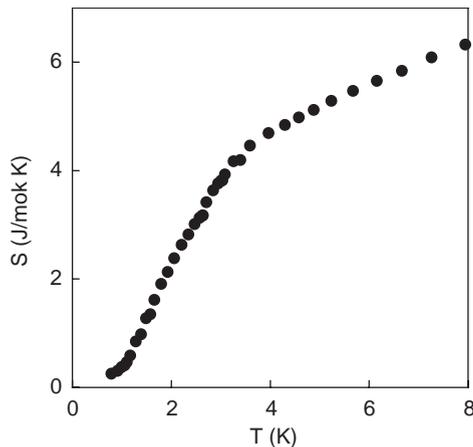


Fig. 6. Temperature dependence of magnetic entropy, reaching $R \ln 2$ near 6 K.

transitions are observed in the magnetic data in Fig. 2, even though the lower-temperature anomaly is less apparent. Finally, the relative areas covered by the two specific heat anomalies in

Fig. 5 appear to be in reasonable agreement with those of the ratio between the two different Er^{3+} sites in the unit cell [7].

In conclusion, two peaks in the specific heat are observed below 3 K in erbium sesquisulfide. They are identified as being associated with an anti-ferromagnetic ordering of two non-equivalent Er^{3+} sublattices in the monoclinic crystal, having T_N near 3 and 2 K, respectively.

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