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Low-temperature calorimetric study of magnetic ordering in erbium oxide

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Low-temperature heat-capacity measurements on erbium oxide show an antiferromagnetic transition at 3.3 K, which is corroborated by magnetic-susceptibility data. Entropy calculations indicate that the magnetic ordering is associated with the ground-state doublet of Er^{3+} ions located at one of their two nonequivalent sites in the cubic crystal.

Rare-earth elements form the basis of a wide range of magnetic alloys and compounds of basic as well as technological importance. They also play a significant role in the current research on high-transition-temperature superconductors. Syntheses of these materials often involve rare-earth oxides in the initial stage, which are thermally decomposed during the various reaction procedures. Minute amounts of these oxides could, however, remain in the final products. It is also possible that oxidation of rare earths would occur during high-temperature processing. Such low-level contaminations can usually be ignored, except in cases where the intended study on a given specimen is calorimetric or magnetic in nature, and the rare-earth oxide impurities undergo magnetic transitions in the temperature range of interest. The knowledge of these transitions then becomes relevant in data analysis and interpretation. Earlier studies of rare-earth oxides exhibiting magnetic ordering include those on, e.g., gadolinium oxide[1,2] and ytterbium oxide.[3] This paper describes the determination calorimetrically of such a behavior in erbium oxide.

The 0.65-g sample, in the form of a pressed and sintered (24 h at 980 °C) disk, was prepared from Johnson Matthey's 99.9%-pure powders. X-ray-diffraction patterns agreed well with those expected for the cubic compound. It was thermally anchored to a thermometer-heater assembly in an adiabatic calorimeter. Heat-capacity measurements were made between 2 and 13 K with pulsed Joule heating and germanium thermometry. Heat capacities of the thermometer-heater assembly alone were separately measured for addenda correction. The overall uncertainty of the results is estimated to be less than 2%.

The results in terms of C versus T are presented in Fig. 1. The heat capacities C have units of J/mol deg, where "mol" (191.26 g) refers to the formula $ErO_{1.5}$ containing one Er^{3+} ion. Also included are data from an earlier work by Westrum and Justice.[4] Their measurements from 300 down to 5 K reveal a Schottky anomaly with a broad peak near 35 K, but the lowest-temperature results are unreliable because of the extrapolated temperature scale for a platinum thermometer calibrated only above 10 K. Otherwise, the two sets of data in Fig. 1 agree reasonably well.

The λ-type anomaly occurs at 3.3 K. This is associated with an antiferromagnetic ordering among Er^{3+} ions. Verification is given in Fig. 2. Magnetic-susceptibility (χ) data from a superconducting quantum interference device (SQUID) magnetometer begin to deviate at 3.3 K from the relation $\chi = C^*/(T+\vartheta)$, where the Curie constant $C^* = 0.033$ cm^3 K/g and the Curie-Weiss temperature $\vartheta = 9.5\ K = 2.9T_N$. An effective magnetic moment of $7.1\mu_B$ can thus be derived for Er^{3+}. Detailed analysis of the magnetic heat capacity requires the subtraction of lattice term (C_L) from the total heat capacity. This relatively small contribution [$C_L = (1.55\times10^{-4}$ J/mol K$^4)T^3$] is approximated by using a same Debye temperature of 315 K as that for isomorphic $GdO_{1.5}$ and

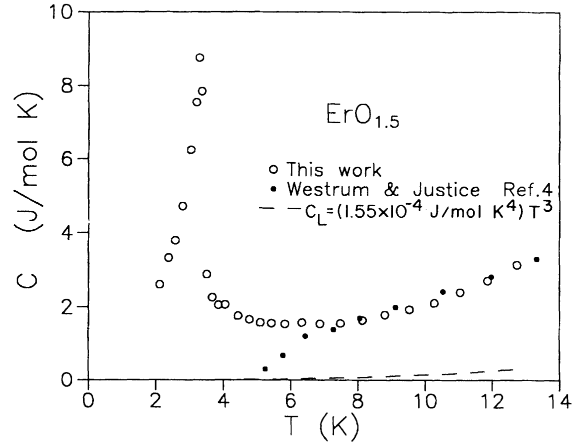

FIG. 1. Temperature dependence of heat capacity. The dashed line represents the estimated lattice contribution based on a Debye temperature of 315 K.

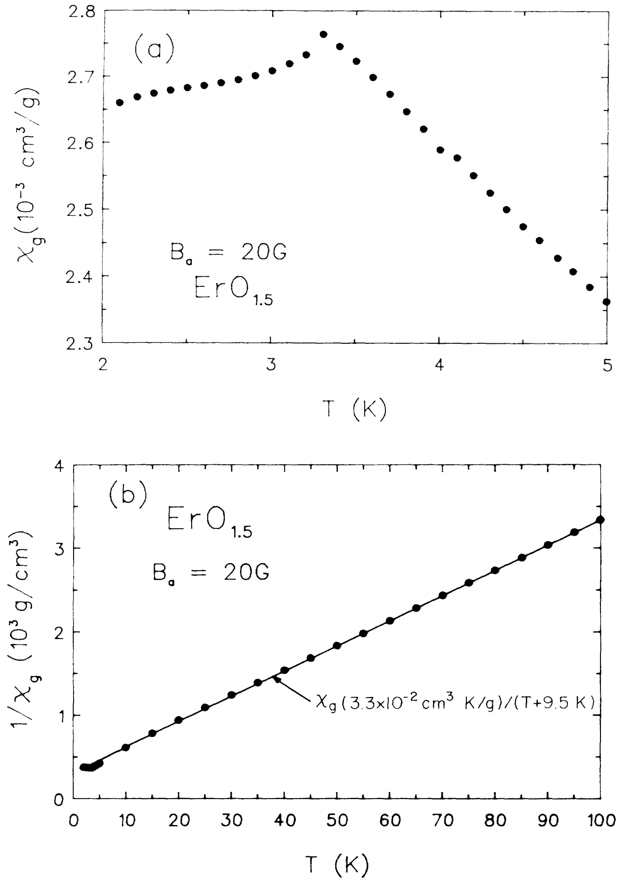

FIG. 2. Temperature dependence of magnetic susceptibility in an applied magnetic field $B_a = 20$ G, showing (a) an antiferromagnetic transition at 3.3 K and (b) a Curie-Weiss fit at higher temperatures.

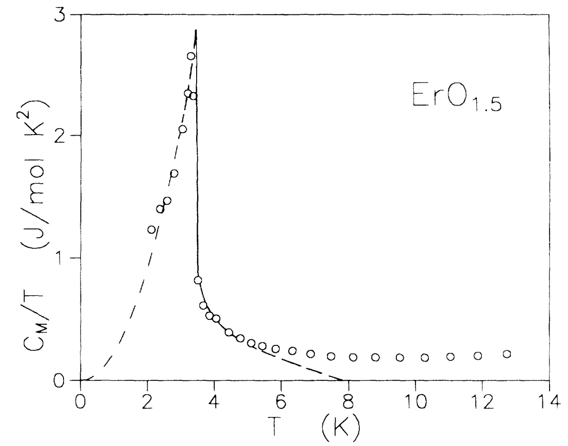

FIG. 3. Temperature dependence of magnetic heat capacity in terms of C_M/T vs T. The dashed lines represent the assumptions based on a T^3 dependence of C_M below T_N and a quick drop-off at higher temperatures. The magnetic entropy change can be evaluated from the area under the curve.

$YbO_{1.5}$.[5] The difference plot in Fig. 3 represents the temperature dependence of C_M/T, where $C_M = C - C_L$. The area under the curve gives magnetic-entropy change $\Delta S_M = \int (C_M/T)dT$. In principle, for Er^{3+} with $J = \frac{15}{2}$, a total magnetic entropy should be R ln16, with R being the gas constant. However, a complete excitation from the ground state requires much higher temperatures than the range being covered here. The magnetic heat capacity in Fig. 3 is likely induced only by the antiferromagnetic ordering with a Néel temperature $T_N = 3.3$ K, plus the low-temperature end of anomalies centered around 35 K or higher.[4] Such anomalies are associated with crystal-field splittings.

Assumptions are made to have a rather quick drop-off for C_M at higher temperatures and $C_M = (0.23$ J/mol K$^4)T^3$ as an approximation below 2.3 K, based on the antiferromagnetic spin-wave model. Entropy associated with the magnetic ordering can now be estimated from Fig. 3 by integrating the area under the smooth curve drawn through the C_M/T data, as well as the dashed-line extrapolations. This gives a ΔS_M value of 4.14 J/mol K between 0 and 8 K, which is smaller than R ln2 = 5.76 J/mol K as expected for a ground-state doublet.[4] The difference is too large to be accounted for by the uncertainties introduced through the data extrapolations.

The more likely explanation to this observation may be as follows: As pointed out by Westrum and Justice,[4] there are two crystallographically nonequivalent Er^{3+} sites in the lattice. Both sites are coordinated to six oxide ions at the corners of a cube, but with the two unoccupied corners located either on a body diagonal (for Er^{3+}-I possessing diagonal axial symmetry) or on a face diagonal (for Er^{3+}-II possessing diagonal axial symmetry), respectively, in the ratio of 1:3. Since the symmetry of the ligand field profoundly affects the splitting of the magnetic ion state, Er^{3+}-I and Er^{3+}-II could have different energy levels. The observed ΔS_M is indeed close to 75% of R ln2. It is therefore concluded that the heat-capacity anomaly at 3.3 K arises from the antiferromagnetic ordering among Er^{3+}-II. Ordering of Er^{3+}-I may occur at temperatures below 2 K. The occurrence of twin-peak anomalies of this type has been reported earlier for isomorphic $GdO_{1.5}$.[2] Similar effects also prevail in many pure rare-earth metals. For example, neodymium has two distinctive ordering temperatures at 8 and 19 K, respectively, for the magnetic moments at two nonequivalent sites in a double-hexagonal-close-packed structure.[6]

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[1] L. T. Crane, J. Chem. Phys. **36**, 10 (1962).

[2] O. V. Lounasmaa, Phys. Rev. **129**, 2460 (1963).

[3] W. E. Henry, Phys. Rev. **98**, 226 (1955).

[4] E. F. Westrum, Jr. and B. H. Justice, J. Phys. Chem. **67**, 659 (1963).

[5] B. H. Justice and E. F. Westrum, Jr., J. Phys. Chem. **67**, 345 (1963).

[6] See, e.g., C. B. Zimm, P. M. Ratzmann, J. A. Barclay, G. F. Green, and J. N. Chafe, Adv. Cryog. Eng. **36**, 763 (1990).