Magnetic susceptibilities and energy levels in Er(OH)$_3$

S. Dasgupta, M. Saha, S. Mroczkowski,* and D. Ghosh

Magnetism Department, Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700032, India

Measurements of the magnetic susceptibilities and their anisotropies of single crystals of Er(OH)$_3$ in the temperature range of 300–70 K are reported here for the first time. Using these results, crystal-field analysis was made to obtain the crystal-field levels of the ground and excited terms, which explained the observed optical spectra. The g values were found to be $g_\parallel = 1.69 \pm 0.01$ and $g_\perp = 8.84 \pm 0.02$. The nuclear hyperfine splitting was also calculated and the hyperfine constants A and B, the internal magnetic field, and the quadrupolar interactions at different temperatures were determined.

I. INTRODUCTION

The rare-earth trihydroxides of Tb^{3+}, Dy^{3+}, and Ho^{3+} showed ferromagnetic ordering around liquid-helium temperatures,[1] and Gd(OH)$_3$ ordered antiferromagnetically at 0.94 ± 0.02 K.[2] However, no ordering was observed in Er(OH)$_3$ even when cooled down to 1.3 K.[3] Thus in the absence of any cooperative phenomena in Er(OH)$_3$ its magnetic and optical properties are completely determined by the interaction of the crystal field, owing to the hydroxyl ions, with the rare-earth cation.

In our previous studies on Tb(OH)$_3$,[4] Ho(OH)$_3$,[5] and Dy(OH)$_3$ (Ref. 6) we noted that the magnetic susceptibilities $K_\parallel$ and $K_\perp$ and their anisotropy $K_\parallel \sim K_\perp$ are very sensitive to crystal-field effects in the temperature range of 300–80 K. It had also been stressed therein that from an analysis of the magnetic data it was possible to obtain, firstly, very accurate values of the crystal-field parameters (CFP), i.e., B_2^0, B_4^0, B_6^0, and B_6^6 which define the crystal-field potential of C_{3h} symmetry at the site of the rare-earth atom and, secondly, the corresponding eigenfunctions of the CF levels of the ground- and excited-state terms. Proceeding in a similar manner in the present work we were able to construct the far-ir and visible spectra and the g values for comparison with the reported data,[3] and also to calculate the hyperfine levels in Er(OH)$_3$ in order to estimate their effects on the magnetic, thermal, and optical properties.

II. EXPERIMENTAL

Single crystals of Er(OH)$_3$, grown by a hydrothermal process,[7] develop as thin prismatic needles along the hexagonal c axis. The space-group symmetry is $P6_3/m$, with two molecular units in the unit cell. The sites being magnetically equivalent, the crystalline susceptibilies χ_c and χ_a ($=\chi_b$) are also the molecular susceptibilities $K_\parallel$ and $K_\perp$, respectively. χ_c being readily detectable, the sign of the anisotropy $K_\parallel \sim K_\perp$ is determined by noting which of the two axes a and c sets along the external magnetic field H. Unlike the other hydroxides studied by us[4-6] it was found that in Er(OH)$_3$, $K_\perp$ is greater than $K_\parallel$. Cooke et al.[8] made a similar observation in erbium ethylsulphate (ErEs).

In these rare-earth hydroxide crystals, the anisotropy becomes comparable [even greater in Tb(OH)$_3$] to the average susceptibility around 80 K.[4-6] Thus, instead of measuring $K_\parallel$ and $K_\perp$ directly we measured the anisotropy $(K_\perp - K_\parallel)$ and $K_\perp$ and determined algebraically $K_\parallel$ and $K_\perp$ with the same order of accuracy. Cooke et al.[8] measured $K_\perp$ and the average susceptibility $\overline{K}$ of ErEs to determine $K_\parallel$ and $K_\perp$ with the same order of accuracy. The anisotropy $(K_\perp - K_\parallel)$ being more sensitive to the crystal field than the average susceptibility, we obtained very accurate values of both $K_\parallel$ and $K_\perp$. The accuracy of the experimental results is better than 10^{-9} emu/mole. Experiments were repeated with six crystals of masses varying between 0.2 and 0.4 mg, and the selection and mounting of crystals were done under a polarizing microscope. The percentage scatter in the values of the anisotropy from crystal to crystal was observed to be very small, i.e., ±0.05%, showing that the single crystals of Er(OH)$_3$ had very few defects. Measurements below liquid-nitrogen temperature were done by boiling under reduced pressure. Details of the measurements of the anisotropy by the static-torque method and the powdered susceptibility by the Faraday method, have been described in our earlier work.[4-6] It is observed that in Er(OH)$_3$ the magnetic anisotropy $(K_\perp - K_\parallel)$ is 6345×10^{-6} emu/mole at 300 K, which is 18% of the average susceptibility. On cooling, this anisotropy increases more rapidly than the average property so that at 70 K the above per-
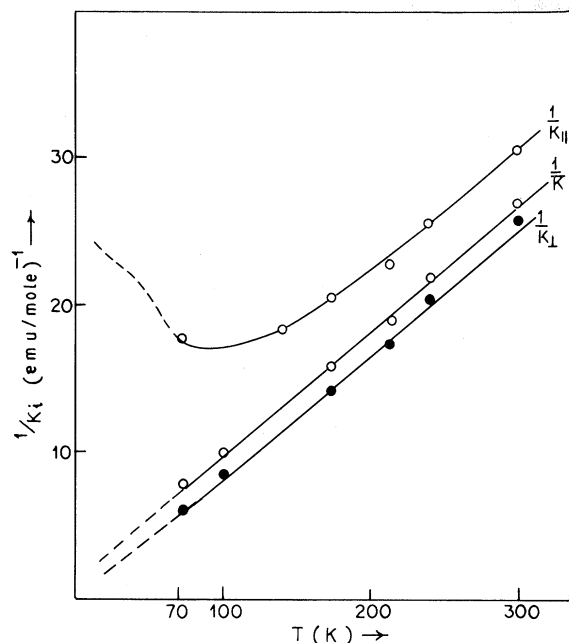
FIG. 1. Thermal variations of $1/K_{\parallel}$, $1/K_{\perp}$, and $1/\bar{K}$ [● — experimental points, ○—calculated points obtained by using anisotropy data (see text); dotted lines are the calculated values using our CFP values].

centage becomes 87%. This is because, on cooling, the $K_{\perp}$ component increases at a faster rate than $K_{\parallel}$ (Fig. 1). This is contrary to that observed in the other hydroxides studied by us. These characteristics are all, of course, owing to the crystal field. In Er(OH)₃, the first- and second-order contributions to $K_{\perp}$ from the different CF levels of the $^4I_{15/2}$ ground multiplet are large. However, only the second-order contributions are effective for $K_{\parallel}$ and this contribution falls off as temperature is lowered due to depopulation of the excited CF levels of the $^4I_{15/2}$ term. The observed thermal variations of $1/K_{\parallel}$, $1/K_{\perp}$, and $1/\bar{K}$ for Er(OH)₃ are shown in Fig. 1. The temperature variations of the susceptibilities obey Curie-Weiss law over a large temperature range as indicated below:

$$K_{\parallel} = 11.875/(T+78.37) \quad (300-120 \text{ K}) \ ,$$

$$K_{\perp} = 11.333/(T-9.07) \quad (300-9 \text{ K}) \ ,$$

$$\bar{K} = 11.666/(T+16.32) \quad (300-20 \text{ K}) \ .$$

The dependence of the Weiss constant on the crystallographic axes directions is the result of CF effects; however, CF effects on the Curie constant are observed to be small because their value is nearly equal to the free-ion value of 11.48. For temperatures below 70 K the calculated values of $1/K_{\parallel}$, $1/K_{\perp}$, and $1/\bar{K}$ are shown by the dotted lines.

III. DISCUSSIONS

Spectral[9] and magnetic studies of several Er³⁺ compounds having LaCl₃ structure have indicated that the lowest free-ion level is $^4I_{15/2}$ followed successively by $^4I_{13/2}$, $^4I_{11/2}$, and $^4I_{9/2}$ at 6700 cm⁻¹, 10 400 cm⁻¹, and 12 500 cm⁻¹, above, respectively.[10] The breakdown of the Landé interval rule indicated that the free-ion levels of Er³⁺ are not pure Russel-Saunders (RS) state but are admixtures of the RS states. The percentage of admixture varied from level to level. For example, the lowest intermediate coupled free-ion state[11] in Er³⁺ is

$$|I_{15/2}\rangle = 0.9838|_3^4I_{20}\rangle - 0.1783|_3^2K_{21}\rangle$$

$$- 0.0191|_3^2L_{21}\rangle \ .$$

For the magnetic properties we need to consider only the ground term $^4I_{15/2}$. The corresponding eigenvalues and eigenfunctions (Table I) are then substituted in the well-known Van Vleck's expression[4] to obtain $K_{\parallel}$ and $K_{\perp}$, where we have used $g_J = 1.196$.[12] The principal susceptibilities $K_{\parallel}$ and $K_{\perp}$ are thus functions of the CF parameters B_2^0, B_4^0, B_6^0, and B_6^6. The experimental data of $K_{\parallel}$, $K_{\perp}$, $\bar{K}$, and $(K_{\perp}-K_{\parallel})$ between 300–70 K were fitted to within 0.01% by using computer programming. Table I includes the parameters obtained by us from the best fit and also those reported by Cone.[3] The sensitive dependence of the anisotropy $K_{\perp}-K_{\parallel}$ on CFP is demonstrated in Fig. 2. Curves 1 and 2 enclose a wide range of values of $T(K_{\perp}-K_{\parallel})$ calculated by varying the values of CFP within the specified errors reported in the optical work.[3] It is seen that the calculated values deviated sometimes from our observed results (dotted line) by a large amount ~ 500 × 10⁻⁶ emu/mole, which is well outside the range of our experimental errors.

A. Optical study

Cone[3] recorded polarized optical spectra of Er(OH)₃ at 77 and 1.3 K. A total of 37 levels were determined from 10 different J manifolds in the visible and far-ir regions. Most of the lines were fairly broad but strong at 77 K and the lines sharpened only slightly at 1.3 K. The energies of three excited levels of the ground manifold $^4I_{15/2}$ ($\mu = \frac{3}{2}, \frac{3}{2}', \frac{1}{2}$) were determined by comparing the transitions originating from the excited levels with those originating from the levels of the ground state. These are listed in Table I. It is seen from the table that these energy values of the excited levels of $^4I_{15/2}$ differ by 3–6 cm⁻¹ from the values calculated with our CFP. Any attempt to make the differences much closer yielded anisotropy values which are definitely outside the range of our experimental errors. However, it is readily seen that our CFP values lie within the errors

BRIEF REPORTS

TABLE I. Crystal-field splitting (in cm^{-1}) of $^4I_{15/2}$ in $Er(OH)_3$. [CFP (in cm^{-1}): $B_2^0 = 186.0$, $B_4^0 = -67.0$, $B_6^0 = -41.0$, $B_6^6 = 521.0$ ($B_2^0 = 192 \pm 6$, $B_4^0 = -64 \pm 3$, $B_6^0 = -40 \pm 1$, $B_6^6 = 521 \pm 8$) (Ref. 3).]

μ	Energy observed[a]	Energy Cone's[a]	calculated Present work	Wave functions (Present work)		
$\frac{5}{2}$	0.0	-1.9	0	$-0.682\| \mp \frac{5}{2} \rangle$	$+0.731\| \pm \frac{7}{2} \rangle$	
$\frac{3}{2}$	61.9	62.1	65.4	$-0.684\| \pm \frac{3}{2} \rangle$	$+0.273\| \pm \frac{15}{2} \rangle$	$+0.677\| \mp \frac{9}{2} \rangle$
$\frac{3}{2}'$	137.8	137.4	134.7	$-0.098\| \pm \frac{3}{2} \rangle$	$-0.954\| \pm \frac{15}{2} \rangle$	$+0.284\| \mp \frac{9}{2} \rangle$
$\frac{1}{2}$	154.3	155.5	160.9	$0.844\| \mp \frac{1}{2} \rangle$	$-0.206\| \mp \frac{13}{2} \rangle$	$-0.495\| \pm \frac{11}{2} \rangle$
$\frac{5}{2}'$		231.4	234.2	$0.731\| \mp \frac{5}{2} \rangle$	$+0.682\| \pm \frac{7}{2} \rangle$	
$\frac{3}{2}''$		277.5	282.2	$-0.723\| \pm \frac{3}{2} \rangle$	$-0.128\| \pm \frac{15}{2} \rangle$	$-0.679\| \mp \frac{9}{2} \rangle$
$\frac{1}{2}'$		330.3	338.3	$0.371\| \mp \frac{1}{2} \rangle$	$-0.443\| \mp \frac{13}{2} \rangle$	$+0.816\| \pm \frac{11}{2} \rangle$
$\frac{1}{2}''$		400.5	408.0	$0.387\| \mp \frac{1}{2} \rangle$	$+0.873\| \mp \frac{13}{2} \rangle$	$+0.297\| \pm \frac{11}{2} \rangle$

[a]Reference 3.

of the CFP values reported from the optical work[3] and thus our CFP values would also explain satisfactorily the visible spectra[3] of $Er(OH)_3$.

B. g values

Scott[13] measured the g values of $Er:Y(OH)_3$ with EPR spectrophotometer at 4.2 K. At this tempera-

ture only the lowest Kramers doublet ($\mu = \pm \frac{5}{2}$) is populated. Using the usual expressions[4,5] for the g values we obtained $g_{||} = 1.693 \pm 0.002$ and $g_\perp = 8.848 \pm 0.004$ which were close to the observed values of $g_{||} = 1.70 \pm 0.05$ and $g_\perp = 8.75 \pm 0.10$ for dilute salt. Cone had noted from his optical studies that the CFP values of pure $Er(OH)_3$ were slightly different from those of the diluted sampels.[3] This then explains the
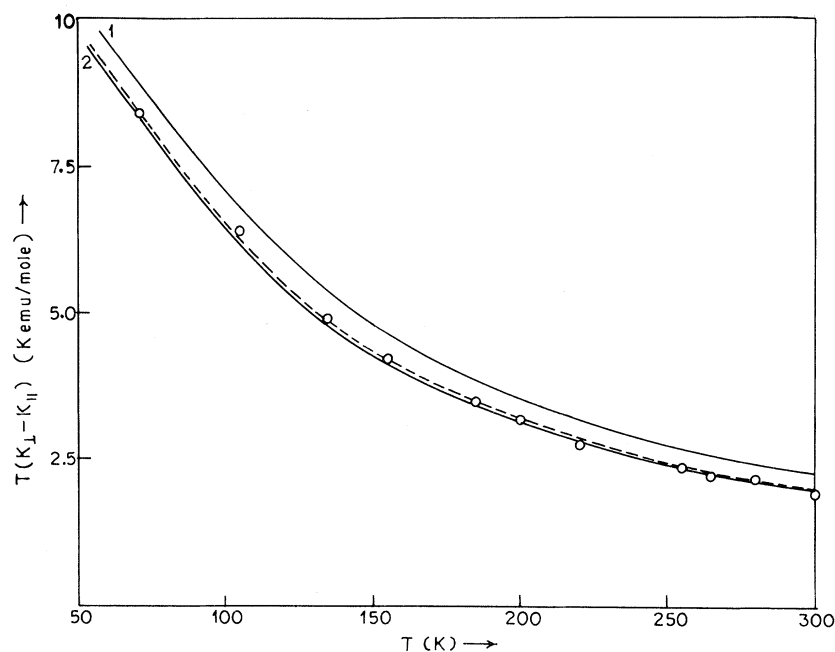

FIG. 2. Thermal variation of $T(K_\perp - K_{||})$ (O—experimental points; the dotted line is the theoretical curve using our CFP values).

small differences in the g values obtained by us from magnetic studies on pure $Er(OH)_3$ crystal from the EPR study on the diluted samples.

C. Nuclear hyperfine effects

Erbium compounds exhibit prominent hyperfine splittings at very low temperature. This is because ^{167}Er, which has a natural abundance of 22.9%, has isotropic spin values of $\frac{7}{2}$ and $\frac{9}{2}$, respectively, for the nuclear ground and first-excited level at 79.32 keV. The total nuclear hyperfine interaction can be written as the sum of nuclear magnetic interaction and nuclear-quadrupole interaction as follows:

$$H_{hf} = AS_z I_z + B(S_x I_x + S_y I_y) + P[3I_z^2 - I(I+1)] \ ,$$

where the symbols have their usual meanings. It is observed that the values of $A/g_{||}$ and $B/g_{\perp}$ in Er^{3+} in ErEs,[14] Er^{3+} in $LaCl_3$,[15] and Er^{3+} in $GdCl_3$ (Ref. 16) remain almost the same. So we determined A and B by substituting known values of $g_{||}$ and $g_{\perp}$. We found $A = (58.20 \pm 0.6) \times 10^{-4}$ cm^{-1} and $B = (310.54 \pm 2) \times 10^{-4}$ cm^{-1} and the internal magnetic field H_{eff} $(= AS_z/g_N \beta_N)$ comes out to be 0.71 ± 0.007 MG.

Using our electronic energy pattern of the ground term, nuclear quadrupole interaction P was calculated by the standard method.[17] We observed that P remains negative throughout the temperature range of 300–1 K and its value changed from -3.100×10^{-4} cm^{-1} at 300 K to -1.025×10^{-4} cm^{-1} at 1 K. The hyperfine splitting was found to be 0.124 cm^{-1} at and below 4 K. The effect of the hyperfine splitting on the susceptibility is consequently very small above this temperature. But this causes a maximum in the specific-heat behavior around 0.055 K. We have found that the hyperfine component of specific heat obeys an inverse T^2 rule, i.e., $C_{hf}/R = 0.0053/T^2$ between 5 and 0.6 K. Experimental studies on specific heat and Mössbauer effect are not yet available in this temperature region, and will be much welcome.

*Present address: Department of Applied Physics, Yale University, New Haven, Conn. 06520.

[1]P. D. Scott and W. P. Wolf, J. Appl. Phys. **39**, 1134 (1968).

[2]A. T. Skjeltorp, C. A. Catenese, H. E. Meissner, and W. P. Wolf, Phys. Rev. B **7**, 2062 (1973).

[3]R. L. Cone, J. Chem. Phys. **57**, 4893 (1972).

[4]D. Ghosh and M. Saha, J. Phys. C **12**, 3803 (1979).

[5]S. Karmakar, M. Saha, and D. Ghosh, J. Appl. Phys. **52**, 4156 (1981).

[6]S. Karmakar, M. Saha, and D. Ghosh, Phys. Rev. B (in press).

[7]S. Mroczkowski, J. Eckert, H. Meissner, and J. C. Doran, J. Cryst. Growth **7**, 333 (1970).

[8]A. H. Cooke, R. Lazenby, and M. J. M. Leask, Proc. Phys. Soc. London **85**, 767 (1965).

[9]G. H. Dieke, *Spectra and Energy Levels of Rare-Earth Ions in Crystals* (Wiley, New York, 1968).

[10]B. G. Wybourne, J. Chem. Phys. **34**, 279 (1961).

[11]S. Hüfner, *Optical Spectra of Transparent Rare-Earth Compounds* (Academic, New York, 1978).

[12]K. Rajnak, J. Chem. Phys. **43**, 847 (1965).

[13]P. D. Scott, dissertation (Yale University, 1970) (unpublished).

[14]R. J. Elliott and K. W. H. Stevens, Proc. R. Soc. London, Ser. A **219**, 387 (1953).

[15]C. A. Hutchinson and E. Wong, J. Chem. Phys. **29**, 754 (1958).

[16]Viswamittar, S. P. Taneja, and S. P. Puri, J. Phys. C **4**, 1692 (1971).

[17]R. G. Barnes, R. L. Mössbauer, E. Kankeleit, and J. M. Poindexter, Phys. Rev. **136**, A175 (1964).