

Magnetic studies on trivalent Er diglycollate $(\text{Na}_3\text{Er}(\text{C}_4\text{H}_4\text{O}_5)_3 \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O})$

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Magnetic studies on trivalent Er diglycollate (Na₃Er(C₄H₄O₅)₃.2NaClO₄.6H₂O)

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Abstract. Measurement of the magnetic susceptibilities and their anisotropy in single crystals of ErDG in the temperature range of 300–22 K are reported here for the first time. The anisotropy value became constant at and below 32 K and this was associated with a possible rotation of each of the three structurally equivalent lanthanide sites in the unit cell without destroying the overall trigonal symmetry of the crystal field (CF), as also observed earlier in NdDG and Gd³⁺:PrDG. CF analysis was performed and the fitted CF parameters were found to be close to the values reported from optical absorption study. The *g*-values were calculated and found to be $g_{\parallel} = 10.314$ and $g_{\perp} = 0.0$. The calculated values of Schottky specific heat showed a maximum at about 100 K.

1. Introduction

One series of Rare Earth complexes which is of special interest in the study of lanthanide chiroptical activity is the RE diglycollate (REDG) system having the general formula Na₃[RE(ODA)₃].2NaClO₄.6H₂O, where ODA denotes the oxydiacetate dianionic ligand –OOCCH₂OCH₂CO–. These REDG crystals have several interesting characteristics which have prompted many to undertake detailed studies of their optical [1–14], magnetic [15–19] and epr [20, 21] properties. Large ligand molecules around the lanthanide keep the heavy ions far apart (interionic separation being 9 Å), making the REDG system magnetically dilute, so CeDG, the first compound in this series, was proposed to be an efficient material for millikelvin thermometry like the widely used cerium magnesium nitrate (CMN) [22]. Moreover the absence of magnetic or dipolar ordering even at very low temperatures makes this system very suitable for crystal field (CF) studies [23, 24, 25]. The RE³⁺O₉ coordination polyhedron in the DG host is a slightly distorted tricapped trigonal prism with trigonal dihedral D₃ symmetry generating a CF with the same symmetry. In the REDG crystals a number forms, eg., trigonal, monoclinic and triclinic, have been isolated [26, 27] in which the site symmetry around the RE ion, though basically the same (i.e. trigonal prism), shows small variations, making them ideal for studying the importance of the CF in the splitting of the energy levels of the rare earth ion in the DG host. The trigonal form of the DG crystals, which has space group *R*32 and D₃ point group symmetry, exhibits optical activity. This provided a great opportunity for studying circular dichroism (c.d.) [2, 7, 9] and optical rotatory dispersion (o.r.d.) properties of the system.

The present study is on the trigonal form of the ErDG crystal, the optical studies of which were reported first by Karmakar *et al* [5] and later by Schoene *et al* [13, 14], Karmakar *et al* [5] studied and assigned some of the CF levels of ${}^2K_{15/2}$ and ${}^2K_{13/2}$ multiplets on the basis of the circular dichroism/optical density (CD/OD) ratio of the spectra taken at 18 K. Schoene *et al* [13, 14] reported CF analysis of absorption spectra between 6000 and 4000 cm^{-1} and CD spectra between 15 000 and 25 000 cm^{-1} of ErDG. Furthermore they observed significant ‘polarization scrambling’ in the spectra below 100 K, which was associated with some structural change around the Er^{3+} ion between room and low temperatures.

From a review of the earlier works on REDG, it is found that some of these crystals undergo an order–disorder phase transition at low temperature [2, 3, 12, 14, 16, 21]. Usually such a phase change reflects an anomalous behaviour of the magnetic susceptibilities, especially in their anisotropic property [28]. A paramagnetic study on single crystals of NdDG between 300 K and 26 K, which was carried out by Dasgupta *et al* [16], revealed a second-order reversible phase change below 74 K. This was associated with the rotation of magnetic susceptibility tensors in the unit cell about the D_3 symmetry axis in such a manner that the overall threefold symmetry was not destroyed.

The present study of the magnetic susceptibilities and anisotropies of ErDG crystal was undertaken as no such study had been reported. This study was expected to verify whether the reported optical CF parameters [14] were able to explain the experimental magnetic susceptibilities and anisotropy results. Since in a Kramers doublet state Jahn–Teller distortion is not possible, ErDG, having a half-integral ground J -state, is a suitable crystal to study the phase change, if any, through its magnetic properties.

2. Experimental results

In the REDG system the rare earth ion is located at sites with D_3 symmetry and each RE^{3+} ion is coordinated to three ODA ligands to form an $\text{RE}(\text{ODA})_3^{3-}$ polyhedron complex. From x-ray studies [24], the unit-cell parameters of ErDG are found to be $a = 9.6988 \text{ \AA}$ and $c = 28.0973 \text{ \AA}$. The unit cell has three molecular units of ErDG, and the D_3 -axis of each is parallel to the c -axis of the trigonal crystal (figure 1). In such a chelate structure, the principal susceptibility tensor K_{\parallel} is expected to be along the c -axis and K_{\perp} in the c -plane [16].

Single crystals of ErDG were prepared by us in the laboratory following the method described by Albertsson [29]. An aqueous solution of Er perchlorate and sodium salts of oxydiacetic acid was mixed in the ratio 1:3. Large pink-coloured single crystals were formed by slow evaporation at room temperature. Recrystallization yielded very good single crystals of ErDG. Four good crystals (2–6 mg) were selected and mounted under a polarizing microscope. The crystals were then coated with collodian solution to prevent decomposition due to loss of water of crystallization in the formula unit, as often occurs when the crystal is cooled more than once.

The mean molar susceptibility $\bar{K} = (K_{\parallel} + 2K_{\perp})/3$ of a powdered sample of ErDG was measured in a sensitive Curie type balance [30] using the Faraday method [31]. At room temperature \bar{K} was $0.03642 \text{ emu mol}^{-1}$ for which the corresponding effective magnetic moment μ_{eff} was $9.35 \mu_B$, which is slightly less than the free ion value, $9.58 \mu_B$, for Er^{3+} obtained from Hund’s formula. The susceptibility \bar{K} increased 6.5-fold at 22 K (figure 2).

The magnetic anisotropy $\chi_c - \chi_a$ (emu gm^{-1}) of the ErDG crystal was measured by the static torque method [32] between 300 and 22 K using a closed-cycle cryogenic system (Displex CS 202) [33]. To measure the magnetic anisotropy the sample was suspended vertically (z -axis) with a very fine quartz fibre (drawn in the laboratory) inside a very stable

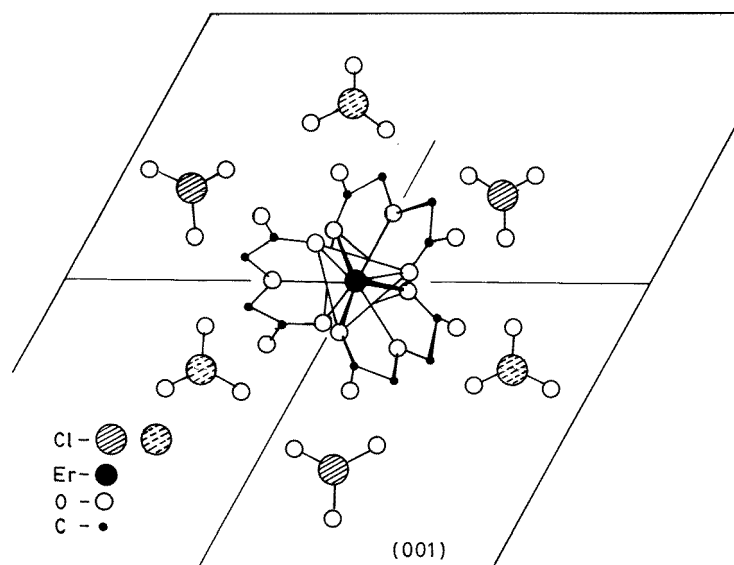


Figure 1. A view along the D_3 -axis of the crystallographic structure of the rare earth ion surrounded by the three diglycollate ligands in ErDG.

and uniform magnetic field (H_x) in such a way that the ac plane of the crystal lay in the horizontal (xy -) plane. When the magnetic field was applied, it was found that the c -axis set parallel to the field direction, suggesting that $\chi_c > \chi_a$ or $K_{\parallel} > K_{\perp}$, throughout the temperature range of our experiment. The error in the experimental results of \bar{K} and ΔK is about 1% around room temperature but decreases by about two orders of magnitude at 40 K because their values increase by large amounts.

At 300 K, the anisotropy $K_{\parallel} - K_{\perp} = \Delta K$ was found to be $0.00158 \text{ emu mol}^{-1}$, which was 4.35% of the average susceptibility \bar{K} . On cooling down to 40 K, ΔK increased to $0.32500 \text{ emu mol}^{-1}$ which was about 150% of \bar{K} at this temperature. However, on further cooling ΔK attained a value of $0.48520 \text{ emu mol}^{-1}$ around 32 K and it remained constant until the lowest attainable temperature which was 22 K (figure 2, inset). For confirmation of such an unusual ΔK - T characteristic, the experiment was repeated with different crystals and with different cooling rates but all crystals showed similar behaviour of the anisotropy.

At 300 K the principal susceptibility of the ErDG crystals in the ab -plane was isotropic. To find out whether any anisotropy developed in this plane, specially below 40 K, the anisotropy experiment was repeated by suspending the crystal with its c -axis vertical, but no anisotropy was found even at the lowest attainable temperature.

From the experimental values of ΔK and \bar{K} , we determined individually the principal magnetic susceptibility components K_{\parallel} and K_{\perp} . It was found that the variation of these components was in accordance with the Curie-Weiss law, $K = C/(T + \theta_p)$ in the higher temperature range as indicated below:

$$\bar{K} = 12.069/(T + 28.96) \quad (300\text{--}110 \text{ K})$$

$$K_{\parallel} = 10.158/(T - 39.62) \quad (300\text{--}110 \text{ K})$$

$$K_{\perp} = 12.888/(T + 63.8) \quad (300\text{--}160 \text{ K}).$$

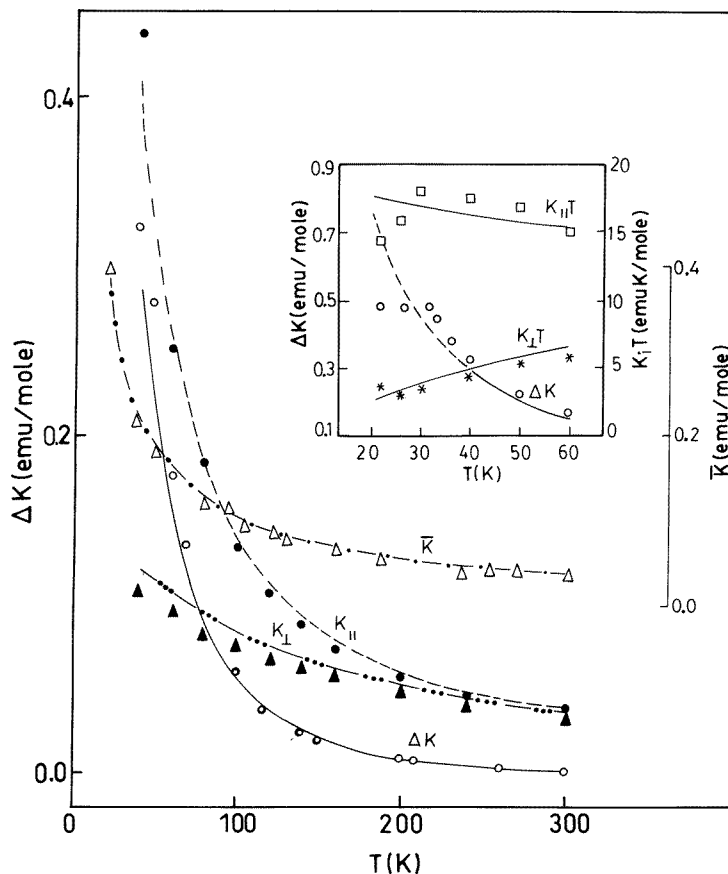


Figure 2. Thermal variations of the observed points and calculated curves of ΔK (\circ , —), $K_{||}$ (\bullet , - - -), K_{\perp} , (\blacktriangle , — · —) (left-hand scale) and \bar{K} (\triangle , — · —). The inset shows the observed anomalous behaviour of ΔK and the consequent effects on the $T K_{||}$ and $T K_{\perp}$ curves between 32 and 22 K.

The Curie constants (C) were close to the free ion value 11.48, but the Weiss constants (θ_P), along and perpendicular to the symmetry axis, were different as a result of the CF effect.

The magnetic experimental results of ErDG between 300 and 40 K showed normal behaviour. Hence it was possible to apply the CF theory to analyse the results and determine the CF parameters, levels and wavefunctions, using which different thermophysical properties were determined as discussed below. However the results between 40 and 22 K exhibited quite different characteristics which could not be explained by CF theory.

3. Discussion

The analysis of the magnetic results between 300 and 40 K was performed by diagonalizing a total Hamiltonian, describing the free ion interactions together with CF interaction in $364|SLJM_J\rangle$ basis states spanning the entire $4f^{11}$ electronic configuration of Er^{3+} . The

free ion Hamiltonian considered is as given below:

$$H_{FI} = E^1 e_1 + E^2 e_2 + E^3 e_3 + \xi \sum_l l_i s_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7). \quad (1)$$

The first three terms are the electrostatic interaction cast in the form due to Racah [34]. The E are combinations of the Slater integrals and the e are angular operators which have been tabulated by Nielson and Koster [35]. The fourth term is the spin-orbit interaction. The last three terms are the two-body interconfiguration interaction terms and $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operators for the groups G_2 and R_7 [23]. Since magnetic susceptibility is a ground term property we have not considered other interactions such as spin-spin, orbit-orbit, spin-other-orbit and three-body electrostatic interactions [25], because the effect of these on the ground level energy pattern is negligible. For Er^{3+} in a DG host the CF part assumed D_3 site symmetry and the corresponding CF Hamiltonian is as follows:

$$H_{CF} = B_{20}U_{20} + B_{40}U_{40} + B_{60}U_{60} + B_{43}(U_{43} - U_{4-3}) \\ + B_{63}(U_{63} - U_{6-3}) + B_{66}(U_{66} + U_{6-6}) \quad (2)$$

where U_{kq} are the one-electron intraconfigurational unit tensor operators and B_{kq} are the even-parity CF parameters [25].

Because of CF interaction, the ground term $^4I_{15/2}$ breaks up into eight Kramers doublets, the positions of which depend on the values of the six CF parameters. These eight eigenvalues and the corresponding eigenfunctions are then used to calculate the magnetic susceptibility according to the Van Vleck susceptibility expression [36],

$$K_j = (g_j^2 N \beta^2 / Z) \sum_i \{[(E_i^{(1)})^2 / kT - 2E_i^{(2)}] \exp(-E_i^{(0)} / kT)\} \quad (3)$$

where $j = \parallel$ or \perp , Z is the partition function, $E_i^{(0)}$, $E_i^{(1)}$ and $E_i^{(2)}$ are the zeroth-, first- and second-order perturbed energies respectively and the other characters have their usual meanings.

The experimental data of \bar{K} , K_{\parallel} , K_{\perp} and $(K_{\parallel} - K_{\perp})$ between 300 and 40 K were fitted as closely as possible using a computer program. The starting parameters were taken as those reported by Schoene *et al* [14]. The free ion parameters were not changed, since the effect of these on the ground term is negligible compared to the optical levels [37]. Using the optical CF parameters [14], the calculated values of ΔK at 300 and 40 K were found to be 0.00442 and 0.2464 emu mol⁻¹ respectively, which differed from the observed values of 0.00158 and 0.3250 emu mol⁻¹. Hence the optical CF parameters had to be changed to match the magnetic results of ΔK , \bar{K} , K_{\parallel} and K_{\perp} between 300 and 40 K.

While fitting the magnetic results by varying the CF parameters, it was observed that the room-temperature (RT) value of ΔK was sensitively dependent on the value of B_{20} . For example, if B_{20} was changed by 1% from the value quoted in table 1, without changing the values of the other parameters shown in the table, then the value of ΔK changed by about 12% at RT, which was far above the experimental error. Similarly it was noticed that the RT value as well as the low-temperature characteristic of each of the other observed quantities depend more sensitively on a particular one or two of the parameters. Thus exhaustive trials had to be performed before arriving at the most satisfactory set of parameters, which is shown in table 1, along with the corresponding ground state energy eigenvalues and eigenfunctions.

Inspection of table 1 shows that the CF parameters were not required to be changed much from the optical values. This is because the spectral study due to Schoene *et al* [14] included the study of properties which depend not only on the positions of the CF levels but

Table 1. The CF splitting (cm^{-1}) and the J mixed CF wavefunctions of the ground term $^4I_{15/2}$ of ErDG with our fitted CF parameters: $B_{20} = -89.0$, $B_{40} = -920.0$, $B_{60} = 374.0$, $B_{43} = -745.0$, $B_{63} = 694.0$, $B_{66} = 620.0$ (all in cm^{-1}) (the free ion parameters are as in [14]).

Energy	Wavefunctions ^a
0.0	$-0.705 {}^4I_{15/2}, \pm 15/2\rangle \pm 0.524 {}^4I_{15/2}, \pm 9/2\rangle - 0.166 {}^4I_{15/2}, \pm 3/2\rangle \pm 0.232 {}^4I_{15/2}, \mp 3/2\rangle$ $-0.232 {}^4I_{15/2}, \mp 9/2\rangle \mp 0.255 {}^4I_{15/2}, \mp 15/2\rangle - 0.118 {}^2K_{15/2}, \pm 15/2\rangle \mp 0.088 {}^2K_{15/2}, \pm 9/2\rangle$ $+0.028 {}^2K_{15/2}, \pm 3/2\rangle \mp 0.039 {}^2K_{15/2}, \mp 3/2\rangle - 0.039 {}^2K_{15/2}, \mp 9/2\rangle \pm 0.043 {}^2K_{15/2}, \mp 15/2\rangle$
47.32	$-0.137 {}^4I_{15/2}, \pm 11/2\rangle \pm 0.580 {}^4I_{15/2}, \pm 5/2\rangle - 0.022 {}^4I_{15/2}, \mp 1/2\rangle \pm 0.704 {}^4I_{15/2}, \mp 7/2\rangle$ $+0.348 {}^4I_{15/2}, \mp 13/2\rangle + 0.023 {}^2K_{15/2}, \pm 11/2\rangle \mp 0.097 {}^2K_{15/2}, \pm 5/2\rangle + 0.003 {}^2K_{15/2}, \mp 1/2\rangle$ $\mp 0.118 {}^2K_{15/2}, \mp 7/2\rangle - 0.058 {}^2K_{15/2}, \mp 13/2\rangle$
151.67	$\pm 0.220 {}^4I_{15/2}, \pm 13/2\rangle + 0.057 {}^4I_{15/2}, \pm 7/2\rangle \pm 0.872 {}^4I_{15/2}, \pm 1/2\rangle - 0.062 {}^4I_{15/2}, \mp 5/2\rangle$ $\pm 0.395 {}^4I_{15/2}, \mp 11/2\rangle \mp 0.037 {}^2K_{15/2}, \pm 13/2\rangle - 0.009 {}^2K_{15/2}, \pm 7/2\rangle \mp 0.147 {}^2K_{15/2}, \pm 1/2\rangle$ $+0.01 {}^2K_{15/2}, \mp 5/2\rangle \mp 0.066 {}^2K_{15/2}, \mp 11/2\rangle$
173.29	$+0.322 {}^4I_{15/2}, \pm 15/2\rangle \pm 0.029 {}^4I_{15/2}, \pm 9/2\rangle - 0.582 {}^4I_{15/2}, \pm 3/2\rangle \pm 0.628 {}^4I_{15/2}, \mp 3/2\rangle$ $-0.204 {}^4I_{15/2}, \mp 9/2\rangle \pm 0.303 {}^4I_{15/2}, \pm 15/2\rangle - 0.054 {}^2K_{15/2}, \pm 15/2\rangle \mp 0.005 {}^2K_{15/2}, \mp 9/2\rangle$ $+0.098 {}^2K_{15/2}, \pm 3/2\rangle \mp 0.106 {}^2K_{15/2}, \mp 3/2\rangle + 0.034 {}^2K_{15/2}, \mp 9/2\rangle \mp 0.051 {}^2K_{15/2}, \mp 15/2\rangle$
212.45	$\mp 0.295 {}^4I_{15/2}, \pm 11/2\rangle + 0.698 {}^4I_{15/2}, \pm 5/2\rangle \pm 0.172 {}^4I_{15/2}, \mp 1/2\rangle - 0.403 {}^4I_{15/2}, \mp 7/2\rangle$ $\mp 0.453 {}^4I_{15/2}, \mp 13/2\rangle \pm 0.05 {}^2K_{15/2}, \pm 11/2\rangle - 0.118 {}^2K_{15/2}, \pm 5/2\rangle \mp 0.029 {}^2K_{15/2}, \mp 1/2\rangle$ $+0.068 {}^2K_{15/2}, \mp 7/2\rangle \pm 0.076 {}^2K_{15/2}, \mp 13/2\rangle$
340.33	$\mp 0.460 {}^4I_{15/2}, \pm 13/2\rangle - 0.201 {}^4I_{15/2}, \pm 7/2\rangle \mp 0.241 {}^4I_{15/2}, \pm 1/2\rangle - 0.209 {}^4I_{15/2}, \mp 5/2\rangle$ $\pm 0.786 {}^4I_{15/2}, \mp 11/2\rangle \pm 0.078 {}^2K_{15/2}, \pm 13/2\rangle + 0.034 {}^2K_{15/2}, \pm 7/2\rangle \pm 0.041 {}^2K_{15/2}, \pm 1/2\rangle$ $+0.035 {}^2K_{15/2}, \mp 5/2\rangle \mp 0.132 {}^2K_{15/2}, \mp 11/2\rangle$
381.95	$\pm 0.413 {}^4I_{15/2}, \pm 15/2\rangle + 0.716 {}^4I_{15/2}, \pm 9/2\rangle \pm 0.053 {}^4I_{15/2}, \pm 3/2\rangle - 0.393 {}^4I_{15/2}, \mp 3/2\rangle$ $\mp 0.296 {}^4I_{15/2}, \pm 9/2\rangle + 0.208 {}^4I_{15/2}, \mp 15/2\rangle \mp 0.07 {}^2K_{15/2}, \pm 15/2\rangle - 0.121 {}^2K_{15/2}, \pm 9/2\rangle$ $\mp 0.008 {}^2K_{15/2}, \pm 3/2\rangle + 0.067 {}^2K_{15/2}, \mp 3/2\rangle \pm 0.05 {}^2K_{15/2}, \mp 9/2\rangle - 0.035 {}^2K_{15/2}, \mp 15/2\rangle$
447.59	$\mp 0.304 {}^4I_{15/2}, \pm 11/2\rangle - 0.318 {}^4I_{15/2}, \pm 5/2\rangle \pm 0.350 {}^4I_{15/2}, \mp 1/2\rangle + 0.519 {}^4I_{15/2}, \mp 7/2\rangle$ $\mp 0.620 {}^4I_{15/2}, \mp 13/2\rangle \pm 0.051 {}^2K_{15/2}, \pm 11/2\rangle + 0.054 {}^2K_{15/2}, \pm 5/2\rangle \mp 0.06 {}^2K_{15/2}, \mp 1/2\rangle$ $-0.088 {}^2K_{15/2}, \mp 7/2\rangle \pm 0.105 {}^2K_{15/2}, \mp 13/2\rangle$

^a Only contributions from the major terms $^4I_{15/2}$ and $^2K_{15/2}$ are shown here.

also the CF wavefunctions. As mentioned above the effects of variations of CF parameters are very prominent on the directional susceptibilities and their anisotropy [38, 39], which explains the deviations between the observed characteristics of these magnetic properties and the corresponding values calculated using the optical parameters. It is relevant to mention here that the magnetic properties depend primarily on the ground term characteristics, but optical levels involve several other excited terms, so the CF parameters obtained from fitting of spectra give average values. Previously it was felt that for fitting of spectra closely, CF values were required to be changed from term to term; however in recent times spin correlation effects on the CF [40, 41] have been very successful in accounting for fitting spectra without considering term variations of the CF.

Figure 3 shows the calculated characteristics of $K_{\parallel}^{(1)}$, $K_{\parallel}^{(2)}$, $K_{\perp}^{(1)}$ and $K_{\perp}^{(2)}$, which are the first- and second-order contributions to the parallel and perpendicular components of the susceptibilities. The contributions from the lowest level φ_0 and φ_1 at 47 cm^{-1} are predominant for $K_{\parallel}^{(1)}$ and $K_{\perp}^{(2)}$, which account for their thermal characteristics. However, in the perpendicular direction φ_0 do not contribute in the first order for which reason $K_{\perp}^{(1)}$ increases only slowly on cooling. In the case of $K_{\parallel}^{(2)}$, the contribution from φ_1 is greater than that due to φ_0 at 300 K but falls off on cooling as the former is depopulated (figure 3). The parallel and perpendicular components of the magnetic moments of ErDG at 300 K are

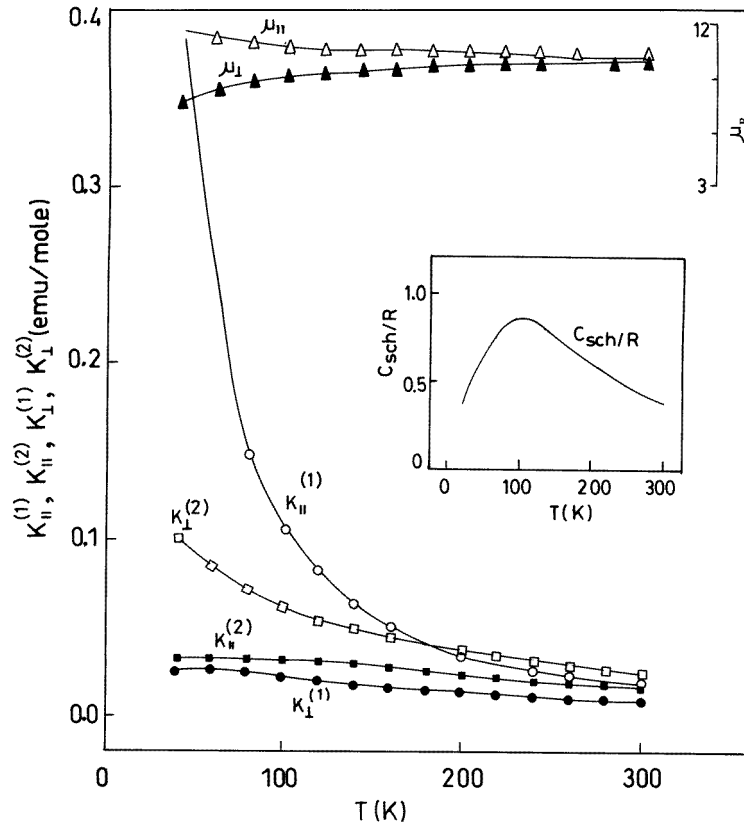


Figure 3. The curves drawn through the calculated points are shown for $K_{||}^{(1)}$ (\circ), $K_{||}^{(2)}$ (\square), $K_{\perp}^{(1)}$ (\bullet), $K_{\perp}^{(2)}$ (\blacksquare), $\mu_{||}$ (\triangle) and μ_{\perp} (\blacktriangle) (see the text). The inset shows the thermal variation of the paramagnetic component of the Schottky specific heat C_{Sch}/R .

$\mu_{||} = 9.65 \mu_B$ and $\mu_{\perp} = 9.35 \mu_B$ respectively. Figure 3 shows that on cooling $\mu_{||}$ increases whereas μ_{\perp} decreases slightly due to the CF effect. The observed thermal characteristics of $K_{||}$ and K_{\perp} are reasonably well matched with the calculated values between 300 and 40 K (figure 2). However, the characteristic of ΔK around 32 K cannot be explained by even large variations of the CF parameters.

To interpret the anomalous behaviour observed in $\Delta K-T$ characteristics around 32 K (figure 2, inset), we tried to find out whether the cause was the same as in the cases of NdDG [16] and $Gd^{3+}:\text{PrDG}$ crystals [21]. The epr studies of $Gd^{3+}:\text{PrDG}$ crystals [21] showed evidence of rotation of each of the three structurally equivalent lanthanide sites in the unit cell by an angle (say θ) about the D_3 -axis. Such a type of rotation was also considered to be the cause of the unusual characteristics of ΔK of NdDG between 74 and 48 K [16]. In the case of such rotation of each of the three Er^{3+}O_9 molecular units in ErDG [16],

$$K_{||} - K_{\perp} = (\chi_c - \chi_a)/(2 \cos^2 \theta - 1). \quad (4)$$

As in NdDG, we assumed that the magnitude of ΔK of Er^{3+}O_9 was not affected by the rotation but the unusual characteristics of $(\chi_c - \chi_a)$ were due to a similar type of rotation. The assumption was based on the fact that earlier epr and optical studies on the REDG crystals did not find much change in the CF level pattern. Thus on substituting the values

of $K_{\parallel} - K_{\perp}$ (dashed curve in the inset of figure 2) which would have been observed if there had been no rotation of the molecular axis, we are able to calculate the angle θ . In the case of $\text{Gd}^{3+}:\text{PrDG}$, the angle was found to be between 15 and 20° [21] and in NdDG it was close to 27° [16]. In the present case it was found that $\theta = 25^{\circ}$ at 22 K. Since measurements could not be made at still lower temperatures, we could not find out whether the rotation increased further on cooling. However, this value of angle $\theta = 25^{\circ}$ in ErDG appears to be quite reasonable when compared with the earlier results. Experimental measurement of g_{\parallel} and g_{\perp} for this system has not been reported until now. Since epr studies of Er^{3+} compounds are easily performed, it is necessary to measure the low-temperature epr signals firstly to determine, the angle of rotation and secondly to find out whether the g -values are changed above and below 40 K.

Using the wavefunctions of CF levels of table 1, we calculated the g -values of ErDG . These values are $g_{\parallel} = 10.314$ and $g_{\perp} = 0.0$, which are very different from those reported for other Er^{3+} compounds [42–44] because in this case the M_j value of the principal component of the lowest level is $15/2$, which is consistent with the optical result [14].

The paramagnetic component of Schottky specific heat, C_{Sch} , had been widely studied by Chirico and Westrum for $\text{RE}(\text{OH})_3$ [45, 46] and by others for different RE compounds [47, 48] in order to determine the low-lying CF levels and entropy and for other interests. We calculated C_{Sch} between 300 and 2 K, using the following standard formula [38], substituting the CF energy pattern of the low-lying levels obtained from our magnetic data analysis:

$$C_{Sch} = \frac{R}{Z^2} \left[Z \sum_{i=1}^n x_i^2 \exp(-x_i) - \left\{ \sum_{i=1}^n x_i \exp(-x_i) \right\}^2 \right] \quad (5)$$

where $x_i = E_i^{(0)}/kT$, Z is the partition function and R is the universal gas constant.

A maximum in the specific heat curve was observed at about 100 K (inset of figure 3). Experimental measurement of C_{Sch} of ErDG and NdDG would be welcome, especially in view of the anomalous anisotropy behaviours observed in these crystals at low temperature. It is expected that the specific heat will indicate maxima at such temperatures, because it is likely that the rotation of the molecular units in the unit cell responsible for such behaviours will influence the internal energies of these crystals. The nature of the phase transition in these REDGs can be thus further established.

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