# Magnetic Circular Dichroism of the Thulium and Erbium Ethyl Sulfate Nonahydrate Crystals

Yoshifumi KATO, Toshikazu NAKAYA, and Toshiyuki NAGAI

*Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657*

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The magnetic circular dichroism and absorption spectra of the thulium and erbium ethyl sulfate nonahydrate crystals have been measured at low temperatures, down to 18 K. The analyses are made for five absorption bands of $Tm(C_2H_5SO_4)_3 \cdot 9H_2O$; the bands from the ground state, $^3H_6$, to the excited states $^3F_3$, $^3F_2$, $^1G_4$, $^1D_2$, and $^3P_1$ of $Tm^{3+}$, and for four bands of $Er(C_2H_5SO_4)_3 \cdot 9H_2O$; the bands from the ground state, $^4I_{15/2}$, to the excited states $^4S_{3/2}$, $^4F_{5/2}$, $^4F_{3/2}$, and $^2G_{9/2}$ of $Er^{3+}$. With the aid of the information about energy levels already obtained, the *g* values of the crystal levels relevant to absorptions are derived from the Faraday parameters; these are in good agreement with those obtained by other methods.

A certain amount of crystal field level data for rare earth crystals has been accumulated by the analysis of the absorption and fluorescence spectra and the Zeeman effect for these crystals.[1,2] By using the knowledge of these well established energy levels, it has been pointed out[3-6] that even when optical absorption bands are too broad to give resolved Zeeman patterns, fairly accurate estimates of the spectroscopic splitting factors (*g* value) in the ground and excited states can be obtained from the magnetic circular dichroism (MCD) spectra.

In the present work, the MCD measurements for five absorption bands of thulium ethyl sulfate nonahydrate, $Tm(C_2H_5SO_4)_3 \cdot 9H_2O$ (Tm(ES)), and four absorption bands of erbium ethyl sulfate nonahydrate, $Er(C_2H_5SO_4)_3 \cdot 9H_2O$ (Er(ES)), have been carried out at low temperatures and the *g* values derived from the MCD are compared with those obtained by other methods.

## Experimental

The procedure of the preparation of the crystals is described in our previous paper.[6] All the absorption and MCD spectra were obtained by a JASCO J-10 spectrophotometer equipped with a permanent magnet of 3.6 kG. The measurements at low temperatures down to 18 K were performed using a metal Dewar vessel, as showh in Fig. 1. The temperature of the crystal packed into a sample cell attached to the tail of the liquid helium vessel was measured by using an Au-Co *versus* chromel thermocouple with one junction pressed directly against the crystal and found to be $80 \pm 1$ and $18 \pm 2$ K at liquid nitrogen and helium temperatures, respectively.

The product of the concentration and path length for a sample was determined from a comparison of the absorption strength of several isolated bands in the crystal with that of the corresponding aqueous solution at room temperature. While this procedure may produce errors in the estimate of the absorption coefficient and the molar ellipticity, this is not a serious matter,[6,7] because the important quantities in our discussion are always the ratios of the Faraday parameters to the dipole strength. The slit width was made as narrow as possible ($\approx$0.01 mm) to resolve an overlapping band, although there was a limitation owing to the characteristic resolving power of the instrument. When the incident light beam was directed along the principal axis of a uniaxial, crystal, no birefringence effect was observed in the present measurement; the base line was flat and well behaved with zero magnetic field. The MCD and absorption data thus obtained are considered to be accurate within 20 percent.

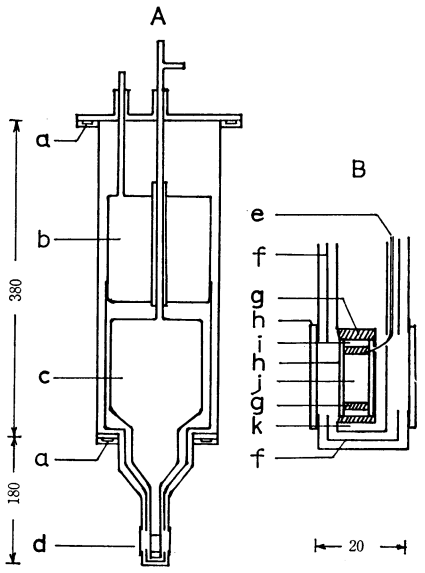


Fig. 1. Metal Dewar vessel for the MCD measurement at liquid helium temperature (A) and the enlarged diagram of its tail part (B). The units are in mm. a: O-ring, b: liquid nitrogen vessel, c: liquid helium vessel, d: sample part, e: thermocouple, f: liquid nitrogen shield, g: indium, h: quartz window, i: sample cell, j: crystal, k: Cu-holder.

## Results and Discussion

*Energy Levels and Calculated* g *Values.* The $Tm^{3+}$ and $Er^{3+}$ ions in ethyl sulfate have $4f^{12}$ and $4f^{11}$ electronic configurations respectively. According to the analysis of the crystal structure of rare earth ethyl sulfates,[8] the space group is $P6_3/m$ ($C^2_{6h}$) and the local symmetry about a rare earth ion is $D_{3h}$ as far as the nearest-neighbor oxygen atoms of 9 crystalline waters are concerned. An ion state $|JM>$ placed in a crystal field splits into several crystal levels, designated by the crystal quantum numbers $\eta$, following Hellwege:[9] *e.g.*, the ground ion state of Tm(ES), $^3H_6$, and that of Er(ES), $^4I_{15/2}$, split into 9 and 8 crystal levels in $D_{3h}$ symmetry, respectively.

In general, it is possible to evaluate theoretically the *g* values of crystal levels. Wong and Richman[10] made

the calculation of the crystal levels of Tm(ES) and their $g$ values. They obtained the root mean square deviation of 118.9 $cm^{-1}$ for 11 ion levels by the operator equivalent method and that of 10.8 $cm^{-1}$ for 21 crystal levels by the first-order perturbation theory. Although the accuracy of the physical quantities calculated depends on that of the wave functions used, the results by Wong and Richman are considered to be fairly reliable. As there has been no calculation for the $g$ values of Er(ES), we have made the crystal field calculation for this crystal[11] in which the configuration interaction for ion levels and complete $J$-mixing for crystal levels are taken into account by means of the tensor method.[12] This calculation has made it possible to fit 22 ion levels with the root mean square deviation of 78.2 $cm^{-1}$ and to fit 50 crystal levels with that of 3.6 $cm^{-1}$. The calculated $g$ values will be utilized in the comparison with those from MCD in the following section.

*MCD Spectra.* The general expressions for the MCD extensively used can be applied to a uniaxial crystal. The ellipticity accompaning an electronic transition is written as

$$\theta = -\frac{4}{3}\gamma N_a[Af_1/\hbar + (B + C/kT)f_0]H, \qquad (1)$$

where the explicit expressions for the Faraday parameters $A$, $B$, and $C$, are given by Stephens.[13,14] The ordinary conditions assumed in the derivation of Eq. 1 (Zeeman energy $\ll$zero-field state separation, line width, and $kT$) are satisfied in the present measurements. The ratios of the Faraday parameters to the dipole strength $D$ $(=(1/d_a)|\langle a|\boldsymbol{m}|j\rangle|^2)$ are related to the $g$ values of the ground $a$ and excited $j$ states in a transition as

$$|A/D| = |g_j - g_a|, \quad |C/D| = |g_a|, \qquad (2)$$

where the Zeeman splitting is taken as $2g\beta H$, since there are no multiplets except the doublet in the ethyl sulfate crystals. The selection rules in $D_{3h}$ symmetry in case of an even and odd number of electrons are given in

TABLE 1. SELECTION RULES FOR CRYSTAL QUANTUM NUMBER $\eta$ IN $D_{3h}$ SYMMETRY

Even number electrons.

| $\eta''\backslash\eta'$ | 0 | $\pm1$ | $\pm2$ | 3 |
|---|---|---|---|---|
| 0 | — | — | $\sigma$ | $\pi$ |
| $\pm1$ | — | $\sigma$ | $\pi$ | $\sigma$ |
| $\pm2$ | $\sigma$ | $\pi$ | $\sigma$ | — |
| 3 | $\pi$ | $\sigma$ | — | — |

Odd number electrons.

| $\eta''\backslash\eta'$ | $\pm1/2$ | $\pm3/2$ | $\pm5/2$ |
|---|---|---|---|
| $\pm1/2$ | — | $\sigma$ | $\sigma, \pi$ |
| $\pm3/2$ | $\sigma$ | $\pi$ | $\sigma$ |
| $\pm5/2$ | $\sigma, \pi$ | $\sigma$ | — |

Table 1,[15] while $\sigma$ polarization can be observed in the present experiment. The energy level diagrams of Tm(ES) and Er(ES) relevant to the present analysis are given in Fig. 2.[1] The MCD and absorption spectra observed are shown in Figs. 3 and 4 for Tm(ES) and Er(ES), respectively. The absorption bands analyzed are five for Tm(ES): $^3H_6 \rightarrow {}^3F_3$, $^3F_2$, $^1G_4$, $^1D_2$, and $^3P_1$, and four for Er(ES): $^4I_{15/2} \rightarrow {}^4S_{3/2}$, $^4F_{5/2}$ $^4F_{3/2}$, and $^2G_{9/2}$.[16] The Faraday parameters derived from the method of moments[14,17] are given in Tables 2 and 3 for Tm(ES) and Er(ES), respectively. We consider that the parameter values by the graphical method by Bodoz *et al.*[18] and the curve fitting method by a least-squares procedure[19] can be also obtained with similar accuracy to those by the moment method when a careful application of these two methods is made.[19]

*Discussion for Tm(ES).* The lowest crystal level of the $^3H_6$ state of Tm(ES) is a non-degenerate level $\eta=0$. The population of the next level ($\eta=\pm1$), which is 32 $cm^{-1}$ higher than the lowest level, is 8 percent of

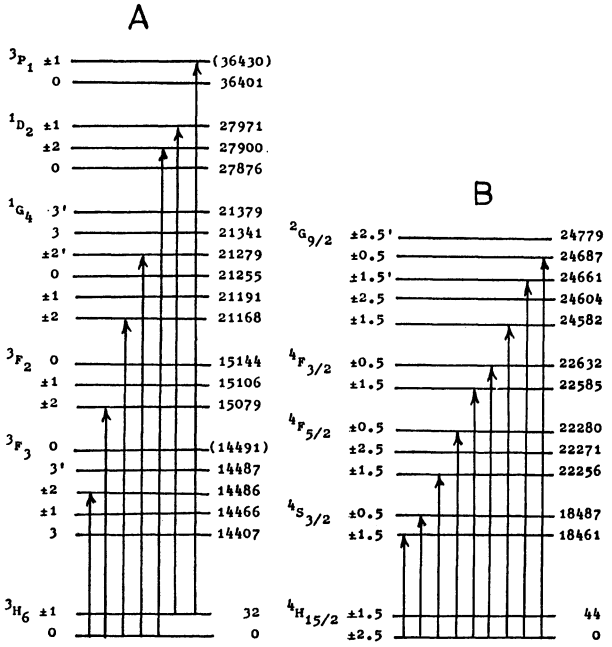


Fig. 2. Energy level diagrams of Tm(ES) (A) and Er(ES) (B) (Ref. 1). The units of energy are in $cm^{-1}$. The values in parentheses are not yet determined experimentally. Allowed transitions are indicated by arrows.

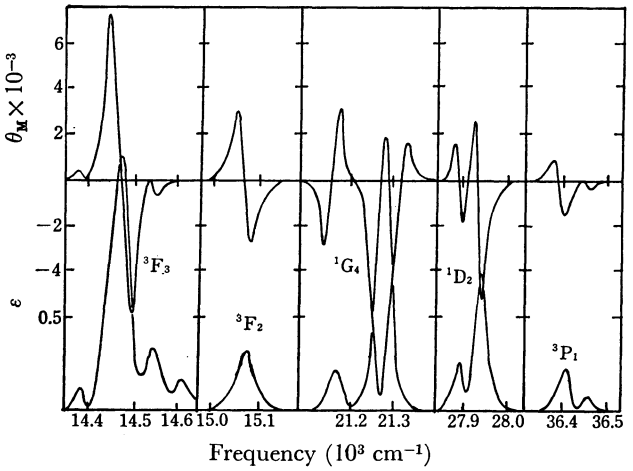


Fig. 3. Absorption and MCD spectra of Tm(ES) at 18 K. $\theta_M$ and $\varepsilon$ are the MCD in molar ellipticity units (degree deciliter $decimeter^{-1}$ $mol^{-1}$) per unit gauss and molar extinction coefficient, respectively.

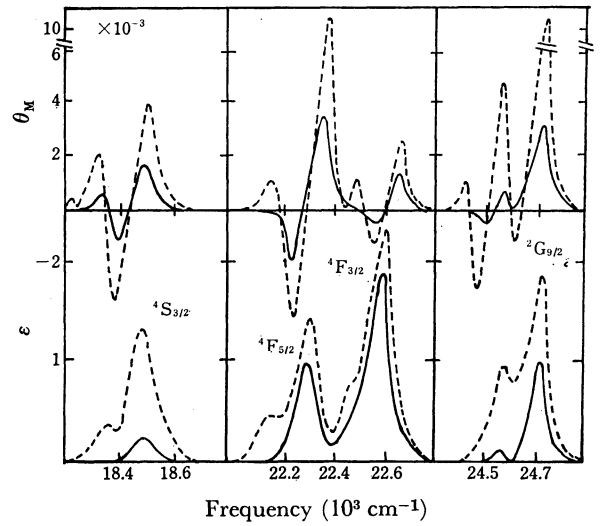


Fig. 4. Absorption and MCD spectra of Er(ES) at 18 K (solid line) and at 80 K (broken line). Notations and units are the same as in Fig. 3.

that of the latter at 18 K. As seen in Fig. 3, the $^3H_6 \rightarrow {}^1D_2$ band splits into two bands: each of these should correspond to the $^3H_6(\eta=0) \rightarrow {}^1D_2(\eta=\pm 2)$ and the $^3H_6(\eta=\pm 1) \rightarrow {}^1D_2(\eta=\pm 1)$ transitions (Fig. 2). Furthermore, the band at about 36400 $cm^{-1}$ is readily seen to be the $^3H_6(\eta=\pm 1) \rightarrow {}^3P_1(\eta=\pm 1)$ transition from the selection rules (Table 1). Thus, the absolute value of $g$ in the $^3H_6(\eta=\pm 1)$ level can be obtained separately from the $C/D$ values in the two transitions from this level; its average value is 1.11 $\beta$. The absolute $g$ values for the excited levels of these two bands are also obtained from the corresponding $A/D$ values. However, for the $^3H_6 \rightarrow {}^3F_3$, $^3F_2$, $^1G_4$ bands, no evident transition from the $^3H_6(\eta=\pm 1)$ level is observed in the present measurements (Fig. 3). If it is assumed that these bands arise solely from the lowest level $^3H_6(\eta=0)$, then all the $C/D$ values for these bands turn out to be zero, the $B/D$ values are fixed, and the absolute $g$ values of the excited levels are obtained from the corresponding $A/D$ values. As a result, all the $g$ values of the crystal levels observed are definitely settled. The $g$ values derived from MCD are compared with those of other methods in Table 4; here the agreement among the three methods is fairly good within the accuracy estimated. The $g$ values from MCD seem to be in better agreement with those by Zeeman effect than are the calculated values.

*Discussion for Er(ES).* All the crystal levels of Er(ES) are doubly degenerate due to the Kramers degeneracy. The lowest crystal level of the $^4I_{15/2}$ state of Er(ES) is $\eta=\pm 5/2$. The population of the next level ($\eta=\pm 3/2$) which is 44 $cm^{-1}$ higher than the lowest level, is 3 percent of that of the latter at 18 K. Thus, we can assume that all the absorption bands at 18 K originate only from the lowest crystal level. However, from the energy level diagram (Fig. 2), each of the bands except the band at about 24580 $cm^{-1}$ should be considered to consist of two transitions to the excited crystal levels ($\eta=\pm 3/2$ and $\pm 1/2$), owing to low dispersion of the instrument used. Therefore, the estimate of $g$ values is not so straightforward. In the $^4I_{15/2} \rightarrow {}^2G_{9/2}$ band consisting of only one transition, the absolute $g$ values for the $^4I_{15/2}(\eta=\pm 5/2)$ and $^2G_{9/2}(\eta=$

Table 2. Faraday parameters divided by dipole strength $D$, central frequency $\nu_0$, and half-width $\Delta$ at $1/e$ of the maximum absorption in Tm(ES) at 18 K

| Transition | $\nu_0$[a,b] ($cm^{-1}$) | $\Delta$ ($cm^{-1}$) | $D$ ($10^{-5}$ $D^2$) | $A/D$ ($\beta$) | $B/D$[b] ($\beta/cm^{-1}$) | $C/D$ ($\beta$) |
|---|---|---|---|---|---|---|
| $^3H_6(0) \longrightarrow {}^3F_3(\pm 2)$ | 14486 | 27 | 2.51 | 1.45 | −0.0011 | 0 |
| $^3H_6(0) \longrightarrow {}^3F_2(\pm 2)$ | 15079 | 25 | 0.560 | −1.34 | −0.0037 | 0 |
| $^3H_6(0) \longrightarrow {}^1G_4(\pm 2)$ | 21168 | 20 | 0.254 | 1.89 | −0.0057 | 0 |
| $^3H_6(0) \longrightarrow {}^1G_4(\pm 2')$ | 21279 | 23 | 2.35 | 0.11 | 0.0205 | 0 |
| $^3H_6(0) \longrightarrow {}^1D_2(\pm 2)$ | 27900 | 13 | 0.121 | −1.23 | 0.0008 | 0 |
| $^3H_6(\pm 1) \rightarrow {}^1D_2(\pm 1)$ | 27939 | 15 | 0.487 | −0.66 | (0) | 1.30 |
| $^3H_6(\pm 1) \rightarrow {}^3P_1(\pm 1)$ | (36400) | 22 | 0.207 | −0.57 | (0) | 0.91 |

a) The data from Ref. 1. b) The values in parentheses are assumed ones.

Table 3. Faraday parameters divided by dipole strength $D$, central frequency $\nu_0$, and half-width $\Delta$ at $1/e$ of the maximum absorption in Er(ES)

| Excited state[a] | $T$ (K) | $\nu_0$ ($cm^{-1}$) | $\Delta$ ($cm^{-1}$) | $D$ ($10^{-5}$ $D^2$) | $A/D$ ($\beta$) | $B/D$ ($\beta/cm^{-1}$) | $C/D$ ($\beta$) |
|---|---|---|---|---|---|---|---|
| $^4S_{3/2}(\pm 3/2, \pm 1/2)$ | 80 | 18470 | 44 | 3.36 | 1.45 | 0.001 | −0.21 |
| | 18 | | 40 | 0.96 | 1.50 | | |
| $^4F_{5/2}(\pm 3/2, \pm 1/2)$ | 80 | 22270 | 54 | 3.71 | 1.39 | 0.013 | −0.26 |
| | 18 | | 40 | 1.97 | 1.02 | | |
| $^4F_{3/2}(\pm 3/2, \pm 1/2)$ | 80 | 22615 | 59 | 4.25 | 0.22 | −0.003 | −0.01 |
| | 18 | | 42 | 4.09 | 0.12 | | |
| $^2G_{9/2}(\pm 3/2)$ | 80 | 24580 | 52 | 0.68 | 2.62 | 0.006 | −0.86 |
| | 18 | | 28 | 0.16 | 2.51 | | |
| $^2G_{9/2}(\pm 1/2, \pm 3/2')$ | 80 | 24670 | 42 | 2.89 | 1.64 | −0.009 | −0.10 |
| | 18 | | 35 | 1.25 | 1.22 | | |

a) The ground state is $^4I_{15/2}(\eta=\pm 5/2)$.

TABLE 4. COMPARISON OF THE $g$ VALUES IN Tm(ES)

| Level Term | $\eta$ | Energy ($cm^{-1}$) | $g$ value MCD[a] | Zeeman[b] | Calcd[c] |
|---|---|---|---|---|---|
| $^3H_6$ | $\pm1$ | 32 | 1.11 | 1.00±0.20 | 0.55 |
| $^3F_3$ | $\pm2$ | 14486 | 1.45 | 1.88±0.10 | 2.17 |
| $^3F_2$ | $\pm2$ | 15079 | 1.34 | 1.46±0.02 | 1.51 |
| $^1G_4$ | $\pm2$ | 21168 | 1.89 | 1.80±0.03 | 1.52 |
| | $\pm2'$ | 21279 | 0.11 | 0.00 | 0.40 |
| $^1D_2$ | $\pm1$ | 27900 | 1.99 | — | 2.27 |
| | $\pm2$ | 27971 | 1.23 | — | 1.14 |
| $^3P_1$ | $\pm1$ | ≈36430 | 1.48 or 0.34 | — | — |

a) The absolute values. b) The data from Ref. 21. c) The data from Ref. 10.

$\pm3/2$) levels can be determined from the Faraday parameters. As seen in Table 3, the $A/D$ values for each of the other four bands are almost constant and independent of temperature, but the $C/D$ values over these bands are not consistent with each other and also are considerably different from the value of the $^4I_{15/2}(\eta=\pm5/2)\rightarrow{}^2G_{9/2}(\eta=\pm3/2)$ band. Therefore it will be difficult to extract useful information from these $C/D$ values. When it is assumed that each $A/D$ value of the above four bands is a simple sum of the values from the two transitions which are contained within a band, and the $g$ value of the ground level is taken as 0.75, being the value from the Zeeman experiment,[20] the $g$ values for the excited crystal level can be estimated. The $g$ values thus obtained are compared with those of other methods in Table 5. The agreement between the $g$ values from MCD and those of other methods is satisfactory, considering the above assumption.

TABLE 5. COMPARISON OF THE $g$ VALUES IN Er(ES)

| Level Term | $\eta$ | Energy ($cm^{-1}$) | $g$ value MCD[a] | Zeeman[b] | Calcd[c] |
|---|---|---|---|---|---|
| $^4I_{15/2}$ | $\pm5/2$ | 0 | 0.86 | 0.75±0.03<br>0.74±0.02[d] | 0.71 |
| $^4S_{3/2}$ | $\pm3/2$ | 18461 | (2.47) | 2.47±0.09 | 2.53 |
| | $\pm1/2$ | 18487 | 1.00 | — | 0.84 |
| $^4F_{5/2}$ | $\pm3/2$ | 22256 | (1.56) | 1.56±0.15 | 1.57 |
| | $\pm1/2$ | 22280 | 0.35 | — | 0.53 |
| $^4F_{3/2}$ | $\pm3/2$ | 22585 | (1.05) | 1.05±0.08 | 1.12 |
| | $\pm1/2$ | 22632 | 0.28 | — | 0.37 |
| $^2G_{9/2}$ | $\pm3/2$ | 24582 | 1.82 | −1.83±0.05 | −2.26 |
| | $\pm3/2'$ | 24661 | (1.50) | −1.50±0.25 | −0.96 |
| | $\pm1/2$ | 24687 | 0.08 | 0.15±0.10 | 0.54 |

a) The absolute values. The values in parentheses are assumed ones. b) The data from Ref. 20. c) The data from Ref. 11. d) The value from paramagnetic resonance (Ref. 22).

In conclusion, it may be stated that with the aid of the knowledge of well-established energy levels, the $g$ values of crystal levels can be estimated with considerable accuracy from MCD, and these values might be better than other calculated ones.

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$$|\Psi\rangle = -0.49152|^4F\rangle+0.43494|^2G(I)\rangle-0.39289|^2G(II)\rangle +0.24835|^4G\rangle+0.26420|^2H(I)\rangle-0.40396|^2H(II)\rangle +0.34670|^4I\rangle.$$

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