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Magnetic circular dichroism for generating crystal wave functions

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Abstract

The $Ln(ODA)_3^{3-}$ complexes are characterized by a D_3-point symmetry of the Ln^{3+} ion. It is illustrated how a specific angular modification of axial ligands towards a superposable D_{3h} configuration is reflected by the magnetic circular dichroism spectra. In particular, the example of the induced electric dipole transition $^5D_2 \leftarrow {}^7F_0$ of Eu^{3+} is considered.

1. Introduction

The absorption and circular dichroism (CD) spectra of $Na_3Eu(C_4H_4O_5)_3 \cdot 2NaClO_4 \cdot 6H_2O$ (EuODA) have been published by Berry *et al.* [1,2]. We recorded the magnetic circular dichroism (MCD) spectra. These results and a comparison with the experiments of Berry *et al.* are reported in ref. 3.

The particular aim of this paper is to show that the MCD spectra are extremely sensitive to small changes in structural distortions, since these distortions influence the crystal field wave functions in a very specific manner. This is illustrated by the example of the induced electric dipole transition $^5D_2 \leftarrow {}^7F_0$ of Eu^{3+} in EuODA.

2. Structure

Single crystals of LnODA are isomorphous. The three $Ln(ODA)_3^{3-}$ complexes per unit cell are characterized by a D_3-point symmetry of the Ln^{3+} ion [4,5]. Each LnO_9 coordination polyhedron is a distorted tricapped trigonal prism in which the top and bottom triangles are not superposable, but twisted relative to each other by an angle $\Delta\varphi$. The symmetry is also lowered from D_{3h} to D_3 (see Fig. 1). Structural data of $Ln(ODA)_3^{3-}$ systems for different Ln^{3+} ions reveal values of $\Delta\varphi$ between ~10° and ~22° [4–6].

3. MCD studies on the transition $^5D_2 \leftarrow {}^7F_0$ for Eu^{3+}

3.1. Experimental MCD-spectrum

The experimental MCD spectrum is given in Fig. 2. After subtraction of the circular dichroism [1,2], an experimental value for the MCD A_1 Faraday parameter can be obtained [3]. The two signals for the $^5D_2 \leftarrow {}^7F_0$ are characterized by a negative A term at 21 436 cm^{-1} ($A_1 = -6.4 \times 10^{-7} D^2\beta$) and a smaller positive A term at 21 485 cm^{-1} ($A_1 = 2.3 \times 10^{-7} D^2\beta$).

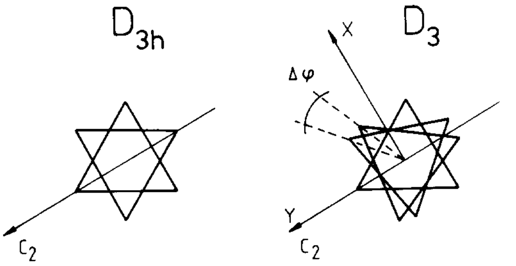

Fig. 1. D_{3h} and D_3 structure viewed down the trigonal axis. $\Delta\varphi$ denotes the angular modification of axial ligands towards a superposable D_{3h} configuration.

3.2. Theoretical discussion

The correlation between the site symmetry and the MCD signal is illustrated in Fig. 3 for both D_{3h} and D_3 symmetry. The crystal field Hamiltonians can be expanded as in (1):

$$H_{D3h}^{\text{even}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_6^6 (C_{-6}^6 + C_6^6)$$

$$H_{D3h}^{\text{odd}} = B_3^3 (C_{-3}^3 + C_3^3) + B_3^5 (C_{-3}^5 + C_3^5) + B_3^7 (C_{-3}^7 + C_3^7)$$

$$H_{D3}^{\text{even}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_3^4 (C_{-3}^4 - C_3^4) + B_3^6 (C_{-3}^6 - C_3^6) + B_6^6 (C_{-6}^6 + C_6^6)$$

$$H_{D3}^{\text{odd}} = B_3^3 (C_{-3}^3 + C_3^3) + B_3^5 (C_{-3}^5 + C_3^5) + B^7 B_3^7 (C_{-3}^7 + C_3^7) + B_6^7 (C_{-6}^7 - C_6^7) \qquad (1)$$

In D_{3h}, the $^5D_2 \leftarrow {}^7F_0$ electric dipole transition is only allowed to the E' level ($M = \pm 2$). Since left circularly polarized light is absorbed to the lowest Zeeman level

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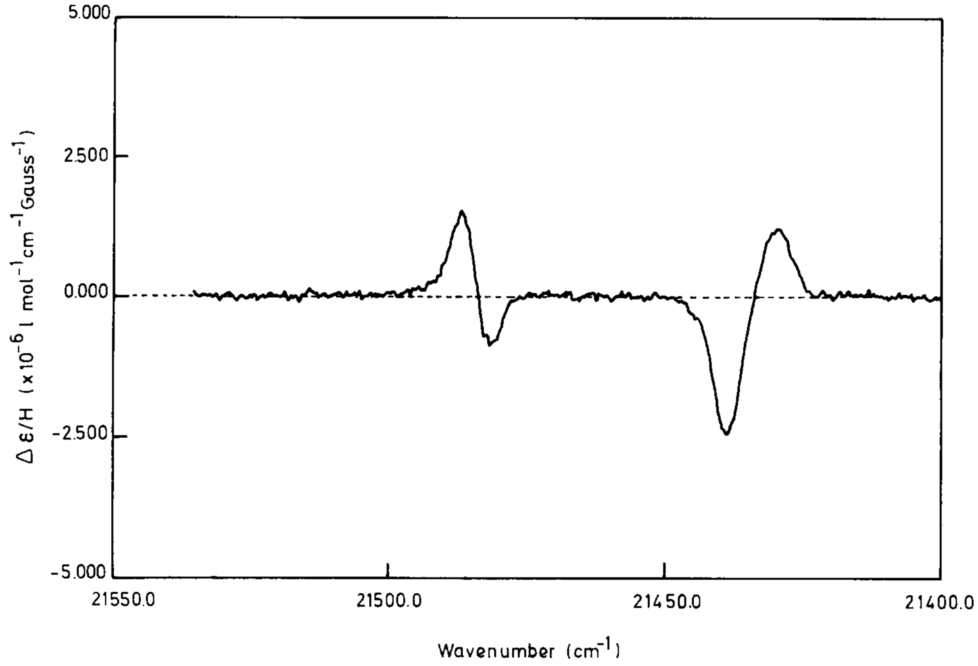

Fig. 2. MCD spectrum of $^5D_2 \leftarrow {}^7F_0$ for Eu^{3+} in EuODA.

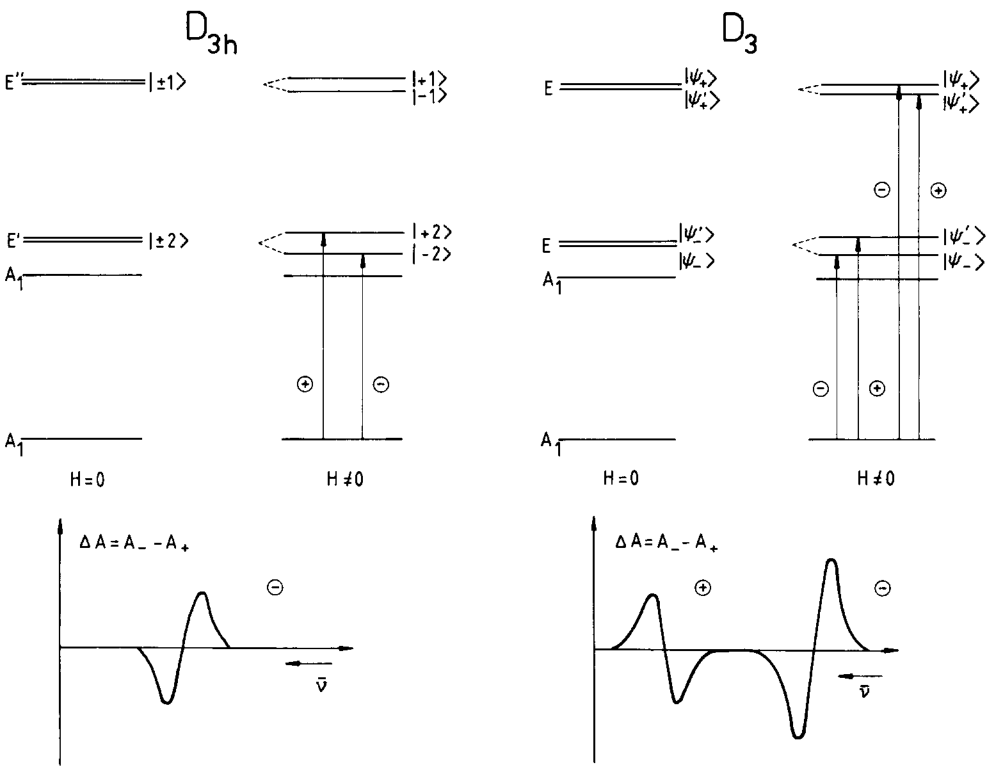

Fig. 3. Correlation between site symmetry and MCD signal for D_{3h} and D_3.

$|-2\rangle$, the MCD results in a negative A term [7]. The distortion from D_{3h} to D_3 results in a mixing of the two E levels by the $B^4_{\pm 3}$ term. Absorption of left circularly polarized light is allowed for the $|-2\rangle$ component by the induced electric dipole mechanism and for the $|+1\rangle$ component by the magnetic dipole mechanism. Consequently, the sign of the A term is determined by the relative energetic positions of the Zeeman levels to which left and right circularly polarized light are absorbed.

The Zeeman energy corresponding to a crystal field function ψ is given by eqn. (2). $\psi=\Sigma_M a_M|M\rangle$

TABLE 1. Influence of the $\Delta\varphi$-distortion on the $k=4$ parameters. ($B_0^4 = -895\ \mathrm{cm}^{-1}$)

	$\Delta\varphi$					
	5°	8° [5]	9.4° [3]	10°	15°	20°
B_3^4/B_0^4	0.433	0.681	0.791	0.837	1.184	1.451
B_3^4	−388	−610	−708	−750	−1060	−1298

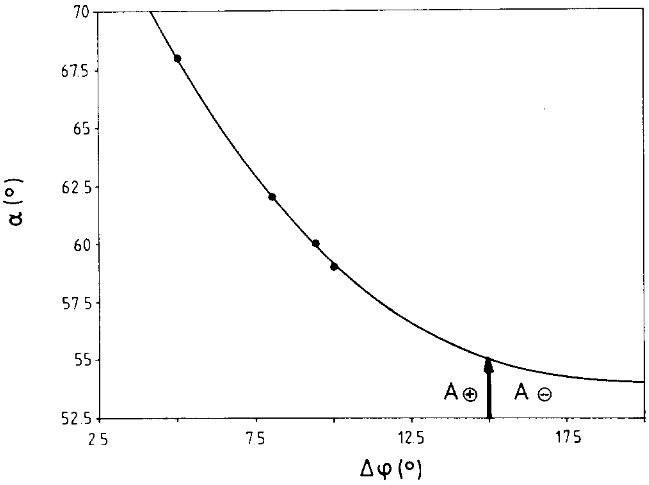

Fig. 4. Mixing parameter α (°) for $|{\sim}2\rangle$ and $|\pm 1\rangle$ components as a function of an angular distortion $\Delta\varphi$ in EuODA, as given by eqn. (3) for $\alpha > 55°$; thus $\Delta\varphi < 15°$, the A term at higher energy (21 485 cm^{-1}) is positive.

with a_M coefficients obtained by crystal field diagonalization

$$E_{\mathrm{Zeeman}} = \langle\psi|L_z + 2S_z|\psi\rangle = g\sum_M |a_M|^2 (M) \tag{2}$$

For the D_3 case, the relative position of the Zeeman levels is a function of the specific mixing by $B^4_{\pm 3}$ of $|-2\rangle$ in $|+1\rangle$ and of $|+2\rangle$ in $|-1\rangle$. This mixing can be described by a mathematical parameter α [8] as given in Appendix A.

Substitution of the wave function expansion in eqn. (2) shows that positive and negative A signals at higher and lower energy, respectively, as found experimentally, are obtained for a mixing parameter

$$55 < \alpha < 125° \tag{3}$$

This is in agreement with the results of a complete crystal field diagonalization [3] revealing a wave function composition with two largest components as given in eqn. (4) corresponding to $\alpha = 59°$.

The upper function mainly contains $|\pm 1\rangle$, while the lower one contains $|\pm 2\rangle$.

$$\begin{aligned} |\psi_+\rangle &= 0.859|+1\rangle + 0.508|-2\rangle \\ |\psi'_+\rangle &= -0.859|-1\rangle + 0.508|+2\rangle \\ |\psi'_-\rangle &= 0.859|+2\rangle + 0.508|-1\rangle \\ |\psi_-\rangle &= 0.859|-2\rangle - 0.508|+1\rangle \end{aligned} \tag{4}$$

Further, a connection can be made between this mathematical mixing parameter α and the specific structural twist angle $\Delta\varphi$, which merely consists of a modification of the polar coordinates of the six axial ligands.

In the framework of an additive crystal field model, the influence of $\Delta\varphi$ on the ratio of the $k=4$ parameters can be calculated. This is shown in Table 1. Introducing this ratio in the crystal field diagonalization results in a mixing parameter α as a function of the $\Delta\varphi$ distortion (see Fig. 4).

An angle $\alpha > 55°$ corresponds on one side to a twist angle $\Delta\varphi < 15°$ and on the other side to a positive MCD signal at high energies.

4. Conclusion

This paper is part of the first complete MCD study on the EuODA complex [3]. In particular, the significant feature of how the MCD signal of a given transition can be related to a geometric angular distortion is illustrated here. For the $^5D_2 \leftarrow {^7F_0}$ transition of Eu^{3+} a positive A term at higher energies indicates that the $\Delta\varphi$ distortion angle is smaller than 15°.

This specific distortion from D_{3h} to D_3 symmetry is also responsible for the optical activity earlier observed in these complexes [1,2].

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Appendix A

The mixing of ψ_A and ψ_B can be described as:

$$|\psi_-\rangle = \sin\alpha|\psi_A\rangle - \cos\alpha|\psi_B\rangle$$

$$|\psi_+\rangle = \cos\alpha|\psi_A\rangle + \sin\alpha|\psi_B\rangle$$

with $\tan 2\alpha \equiv 2H_{AB}/H_{AA} - H_{BB}$ where H_{AA}, H_{BB} are diagonal matrix elements and H_{AB} are non-diagonal matrix elements. Attention is drawn to the footnote in [8], restricting 45° $< \alpha <$ 135°.