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Magneto-optical study of $LaF_3:Eu^{3+}$

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Abstract

The polarised absorption spectra of the Eu^{3+} ion in a LaF_3 host are registered at 4.2 K and room temperature in the spectral region of 380–2100 nm. Magnetic circular dichroism spectra of $LaF_3:Eu^{3+}$ are registered at 4.2 K and room temperature between 400 and 700 nm. The magnetic field has a strength of 6.2 T. The free ion parameters and the crystal field and intensity parameters representative for the C_2 site symmetry, are optimised in a least-squares fitting of experimental against calculated values of the energies and dipole strengths. The optimised set of parameters is then evaluated by simulating the polarised absorption and magnetic circular dichroism spectra. © 1998 Elsevier Science S.A.

Keywords: $LaF_3:Eu^{3+}$; Polarised absorption; Intensities; Magnetic circular dichroism

1. Introduction

Optical absorption spectra of $LaF_3:Eu^{3+}$ were recorded by Kumar et al. [1] at liquid nitrogen temperature in the region 400–900 nm. Transitions in the infrared region from $^7F_0$ to higher ^7F_J levels are mentioned by Weber [2] but no further details are given.

Several authors [3–5] have assumed a D_{3h} point group symmetry. However, the experimental optical data, obtained for rare earth ions with an even number of f electrons, indicate that the rare earth ion occupies a site of low symmetry because all degeneracy is removed. Therefore the point groups C_{2v} [1,6] or C_2 [7] are used. Reference [8] indicates in a qualitative way that the C_2 point group symmetry has to be assumed for a thorough analysis of the experimental data of $LaF_3:Eu^{3+}$.

2. Structural data

LaF_3 has the tysonite structure with space group $P\bar{3}c1$ ($Z=6$) [9,10]. The La^{3+} ions in LaF_3 are situated at a site of C_2 symmetry. Each La^{3+} ion is surrounded by 11 F^- ligands. The coordination polyhedron is a distortion of a tricapped trigonal prism with two extra ligands on the 3-fold axis. There are six sites with identical electric environment oriented in three directions separated by angles of 60° [11]. The *z*-axes of the C_2 sites are perpendicular to the *z*-axis of the crystal and the *x*-axis of each site is parallel to the *z*-axis of the crystal.

3. Experimental details

The single crystal of LaF_3 containing 1% europium measures $10\times7\times7$ mm^3. The principal axis is parallel to one of the 7-mm sides.

The polarised absorption spectra of $LaF_3:Eu^{3+}$ are registered using an AVIV 17 DS spectrophotometer. The optical region of 380–2100 nm is investigated at 4.2 K and room temperature. At 4.2 K, transitions are observed from the $^7F_0$ ground level to the $^7F_6$, $^5D_1$ and $^5D_2$ levels. Transitions to higher energy levels cannot be detected due to the strong and broad absorption band of Eu^{2+} between 300 and 380 nm. At room temperature the transition from $^7F_1$ to $^5D_0$ is also observed.

The magnetic circular dichroism (MCD) spectra are recorded with an AVIV 41 DS CD spectrophotometer, equipped with a superconducting magnet. The optical region of 400–700 nm is investigated at 4.2 K and room temperature with a magnetic field of 6.2 T applied along the *z*-axis of the crystal.

4. Data analysis and spectra simulation

4.1. Energy levels

The energy levels associated with the $4f^6$ electronic

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Table 1
Free ion and crystal field parameters for LaF_3:Eu^{3+}

Parameter	Value (cm^{-1})	Parameter	Value (cm^{-1})[a]	Value (cm^{-1})[b]
E_{ave}	63 895	B_0^2	−256	200
F^2	83 046	B_2^2	59	0
F^4	(58 963)	$B_2^{2\prime}$	0	128
F^6	(42 353)	B_0^4	402	−619
α	(20.16)	B_2^4	496	222
β	(−557)	$B_2^{4\prime}$	−4	150
γ	(1500)	B_4^4	−361	−80
T^2	275	$B_4^{4\prime}$	236	493
T^3	(40)	B_0^6	(937)	−221
T^4	(60)	B_2^6	(−93)	427
T^6	(−300)	$B_2^{6\prime}$	(60)	−433
T^7	(370)	B_4^6	(−20)	102
T^8	(320)	$B_4^{6\prime}$	(−314)	−329
ζ_{SO}	1342	B_6^6	(124)	−101
M^0	3.55	$B_6^{6\prime}$	(318)	−379
M^2	(1.99)			
M^4	(1.35)			
P^2	(360)			
P^4	(270)			
P^6	(180)			

Parameter values shown in brackets are not freely varied.
[a] Set of crystal field parameters in the site coordinate system.
[b] Set of crystal field parameters in the crystal coordinate system.

Table 3
Intensity parameters for LaF_3:Eu^{3+}

Parameter	Value (10^{-12} cm)	Parameter	Value (10^{-12} cm)
A_{211}	−114i	A_{651}	(59i)
A_{231}	17i	A_{652}	(171i)
A_{232}	−53i	A_{653}	(−133i)
A_{233}	101i	A_{654}	(24i)
A_{431}	(−57i)	A_{655}	(−98i)
A_{432}	(−147i)	A_{671}	(−9i)
A_{433}	(−44i)	A_{672}	(−9i)
A_{451}	(19i)	A_{673}	(17i)
A_{452}	(55i)	A_{674}	(7i)
A_{453}	(−42i)	A_{675}	(−12i)
A_{454}	(8i)	A_{676}	(1i)
A_{455}	(−31i)	A_{677}	(−20i)

Parameter values shown in brackets are not optimised.

configuration of Eu^{3+} are analysed in terms of the Hamiltonian: $H=H_0+H_{CF}$. The free ion Hamiltonian H_0 is defined by Crosswhite and Crosswhite [12] and contains 20 parameters. The crystal field Hamiltonian for the C_2 symmetry contains 15 B_q^k parameters. The coordinate system is chosen so that the imaginary crystal field parameter $B_2^{2\prime}$ becomes zero.

A least-squares fitting of the experimental energies, listed in Table 2, against calculated energies is started using the free ion parameters from Ref. [6] and the crystal field parameters from Ref. [7]. The experimental energy levels are not sufficient to support an analysis in which all parameters can be freely varied. The F^k, P^k and M^k parameters are constrained to the following relationships [6,12]: $F^4/F^2=0.71$, $F^6/F^2=0.51$, $P^4/P^2=0.75$, $P^6/P^2=0.50$, $M^2/M^0=0.56$, $M^4/M^0=0.38$. The final set is presented in Table 1. Two sets of crystal field parameters are given. For the first set the coordinate system coincides with the site coordinate system, for the second set the principle axis is parallel to the *z*-axis of the crystal. The use of these two different sets has no effect on the energy levels. But in an intensity calculation the second set has to be used in order to be able to compare calculated with experimental intensities. The experimental and calculated energy levels are summarised in Table 2.

4.2. Intensity calculation

Intensity calculations are expressed in terms of electric dipole (ED) and magnetic dipole (MD) matrix elements. For the evaluation of the MD matrix elements only the composition of the eigenfunctions has to be known [13]. For the calculation of the ED matrix elements a set of intensity parameters $A_{\lambda tp}$ is introduced in the framework of Judd–Ofelt theory [14]. The local field corrections are considered as constants: $\chi_{ED}=1.44$ and $\chi_{MD}=1.60$.

Table 2
Experimental and calculated energy levels for LaF_3:Eu^{3+}

Energy level	E_{exp} (cm^{-1})	E_{calc} (cm^{-1})	Energy level	E_{exp} (cm^{-1})	E_{calc} (cm^{-1})
$^7F_0$ (Γ_1)	0	−6	$^7F_6$ (Γ_1)	(5071)	5059
$^7F_1$ (Γ_1)	313	322	$^7F_6$ (Γ_2)	(5057)	5066
$^7F_1$ (Γ_2)	373	382	$^7F_6$ (Γ_1)	(5092)	5111
$^7F_1$ (Γ_2)	410	408	$^7F_6$ (Γ_2)	(5142)	5113
$^7F_6$ (Γ_1)	(4847)	4853	$^5D_0$ (Γ_1)	17 293	17 297
$^7F_6$ (Γ_1)	(4862)	4858	$^5D_1$ (Γ_1)	19 043	19 040
$^7F_6$ (Γ_2)	(4903)	4910	$^5D_1$ (Γ_2)	19 056	19 053
$^7F_6$ (Γ_2)	—	4918	$^5D_1$ (Γ_2)	19 063	19 065
$^7F_6$ (Γ_1)	—	4933	$^5D_2$ (Γ_2)	21 509	21 511
$^7F_6$ (Γ_2)	(4962)	4958	$^5D_2$ (Γ_1)	21 513	21 519
$^7F_6$ (Γ_1)	(5003)	5001	$^5D_2$ (Γ_2)	21 531	21 537
$^7F_6$ (Γ_2)	(5016)	5021	$^5D_2$ (Γ_1)	21 542	21 542
$^7F_6$ (Γ_1)	—	5039	$^5D_2$ (Γ_1)	21 565	21 551

The irreducible representations for the C_2 point group are shown in brackets. Energy values shown in brackets are not used in the fitting procedure. $\sigma=13$ cm^{-1}.

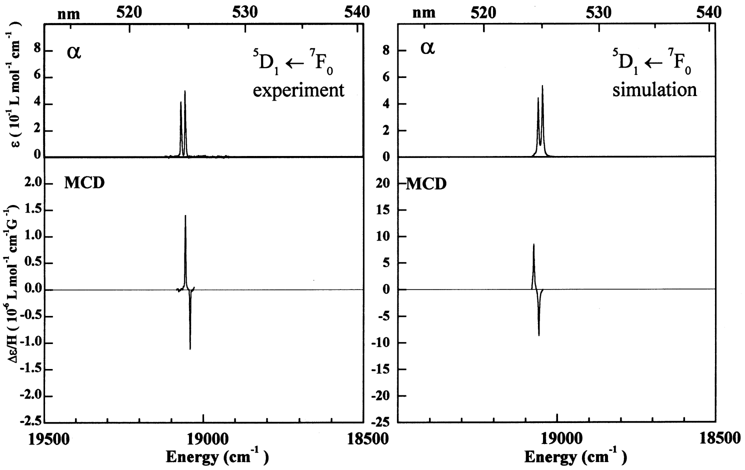

Fig. 1. Experimental (left) and simulated (right) α polarised absorption and MCD spectra of the $^5D_1 \leftarrow {}^7F_0$ transition of LaF$_3$:Eu^{3+} at 4.2 K and with a magnetic field (MCD) of 6.2 T.

In the C_2 site symmetry there are 24 independent $A_{\lambda tp}$ parameters. Starting values for these parameters are calculated from the A_q^k values from [11] and the radial integrals from [15]. Secondly, they are transformed from site to crystal coordinate system so that calculated dipole strengths can be compared with experimental values. In the least-squares fitting only four $A_{\lambda tp}$ parameters with $\lambda=2$ can be optimised, since only the experimental dipole strengths of the transition $^5D_2 \leftarrow {}^7F_0$ can be used in the fitting procedure. The final set of intensity parameters is given in Table 3.

Absorption spectra in α polarisation are graphically simulated for the three transitions according to Ref. [16]. They are presented in Figs. 1–3.

4.3. MCD simulation

The computer programs used Ref. [17] are designed to diagonalise the complete Hamiltonian, incorporating now, besides the free ion and crystal field part, also the Zeeman perturbation. The resulting wave functions are then used to calculate the line strengths of the left and right circularly polarised light components for transitions between the Zeeman levels. Finally the MCD spectrum is simulated according to Ref. [16].

5. Results and discussion

The results of the calculated energy levels, absorption intensities (α) and intensities for transitions between Zeeman levels (MCD) are now used to simulate the spectra. Since the mechanisms that determine the linewidths of the experimental transitions cannot be rationalised to attach some fixed values, it was chosen here to let the linewidth values vary between some reasonable constraints based on the experimental absorption and MCD peaks in the same region.

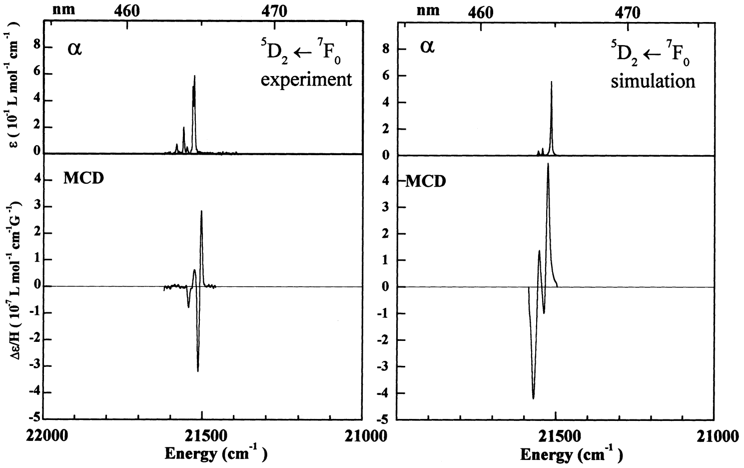

Fig. 2. Experimental (left) and simulated (right) α polarised absorption and MCD spectra of the $^5D_2 \leftarrow {}^7F_0$ transition of LaF$_3$:Eu^{3+} at 4.2 K and with a magnetic field (MCD) of 6.2 T.

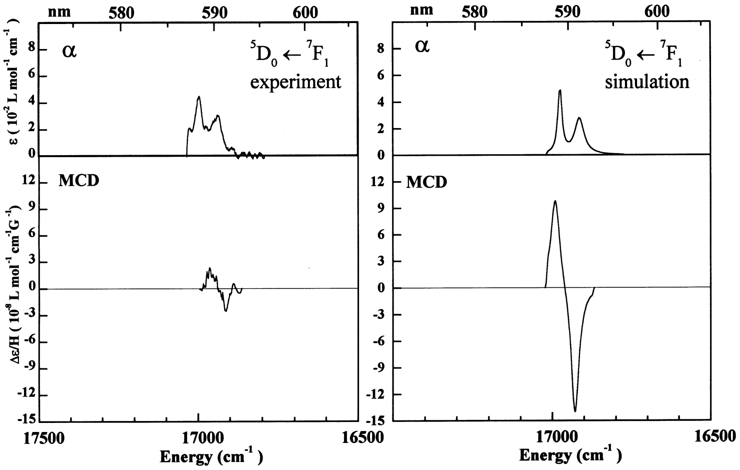

Fig. 3. Experimental (left) and simulated (right) α polarised absorption and MCD spectra of the $^5D_0 \leftarrow {}^7F_1$ transition of LaF_3:Eu^{3+} at room temperature and with a magnetic field (MCD) of 6.2 T.

The transition $^5D_1 \leftarrow {}^7F_0$ (Fig. 1) is a MD transition. The dipole strengths are independent of the $A_{\lambda tp}$ parameters. The good simulation of the α polarised absorption spectrum reflects the optimisation of the crystal field parameters with $k=2$. In the simulated MCD spectrum the signs can be reproduced, but the absolute magnitudes seem to be too big.

The transition $^5D_2 \leftarrow {}^7F_0$ (Fig. 2) is an ED transition. The simulation illustrates the difficulties in the intensity fitting: only four of the 24 parameters can be optimised. For the simulation of the α polarised absorption spectrum the dipole strengths of three transitions are calculated too small, so that only three out of five signals are visible in the simulated spectrum. The signs of the MCD spectrum are nevertheless well simulated, but the relative intensities are somewhat worse.

The transition $^5D_0 \leftarrow {}^7F_1$ (Fig. 3), a MD transition, shows very low experimental intensities. The α polarised absorption spectrum is well simulated. The signs of the MCD signals can be reproduced, but the absolute magnitudes seem to be too big.

The transition $^7F_6 \leftarrow {}^7F_0$ (Fig. 4) could only be detected in polarised absorption, not in MCD because of instrumental limitations. Because the crystal field parameters with $k=6$ and the intensity parameters with $\lambda=4,6$ could not be optimised, no graphical simulations are made. Therefore Fig. 4 presents the α, π and σ polarised absorption spectra for this transition.

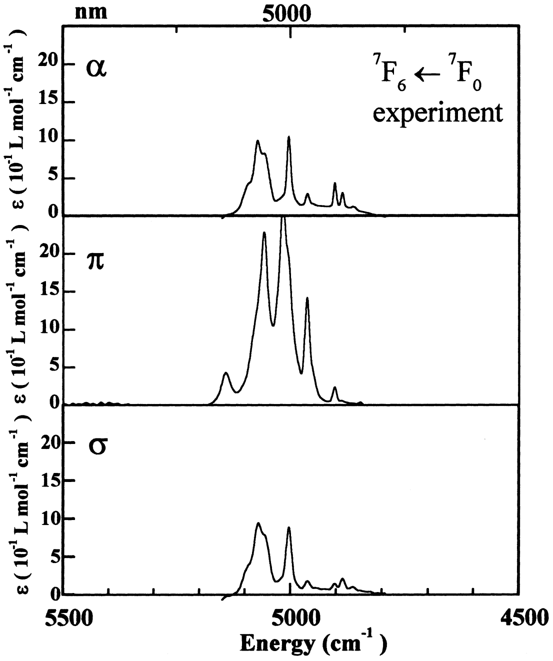

Fig. 4. Experimental α, π and σ polarised absorption spectra of the $^7F_6 \leftarrow {}^7F_0$ transition of LaF_3:Eu^{3+} at 4.2 K.

6. Conclusions

In this paper the α, π and σ polarised absorption and MCD spectra of LaF_3:Eu^{3+} are reported. At 4.2 K three transitions are detected: $^5D_1 \leftarrow {}^7F_0$, $^5D_2 \leftarrow {}^7F_0$ and $^7F_6 \leftarrow {}^7F_0$. The last one, that is registered in the near infrared region, has not been reported earlier. At room temperature one additional transition is registered: $^5D_0 \leftarrow {}^7F_1$.

A set of free ion, crystal field and intensity parameters is optimised in a least-squares fitting of experimental against calculated values of the crystal field energies and dipole strengths. In Refs. [6,7], experimental information about the irreducible representations was not introduced as a constraint on the energy fitting. In this article, however, the characteristics of the wave functions, which could be identified by polarised absorption, are actually taken into account. This results in a much better fitting of the $^5D_1$ and $^5D_2$ levels. Due to the small number of experimental data, the crystal field parameters with $k=6$, and the intensity parameters with $\lambda=4,6$ cannot be optimised. This is the reason why the intensities are not always well simulated.

Since the fitting procedure does not include any MCD data, the graphical simulation of these spectra is a test of the quality of the optimised parameter set. With our set of parameters the signs of the MCD signals can be reproduced.

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