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Crystal-field analysis of Eu^{3+} in LiYF_4

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Abstract. Polarized absorption spectra of Eu^{3+} in single-crystal LiYF_4 have been recorded at 298 K and 77 K in the region from 3900–39 000 cm^{-1} . Symmetry assignments have been made in both D_{2d} and S_4 . Calculated energy levels are obtained by diagonalizing a parametric Hamiltonian that describes the free-ion and crystal-field interactions in a basis of states spanning the $4f^6$ electronic configuration of Eu^{3+} . J mixing was taken into account.

1. Introduction

Lithium yttrium fluoride, LiYF_4 , is an attractive host crystal for the spectroscopic investigation of triply ionized lanthanide ions in crystal fields. Because Ln^{3+} can replace Y^{3+} at the same site, no charge compensation is required. Crystals of LiYF_4 are transparent over a wide spectral region from about 220 nm in the UV to 8 μm in the IR [1]. They are stable against air and moisture. The spectroscopic properties of LiYF_4 doped with Ln^{3+} ions have been reviewed by Morrison and Leavitt [2] and by Jayasankar *et al* [3].

Eu^{3+} -doped LiYF_4 was not investigated until 1985 [4], because of the difficulties in growing $\text{LiYF}_4\cdot\text{Eu}^{3+}$ single crystals of a reasonable size. The spectroscopic properties of Eu^{3+} in LiYF_4 in the region from 0 to 19 040 cm^{-1} were first determined by our group [4, 5] using fluorescence data. Bihari *et al* [6] extended this work and recorded the absorption spectra up to 25 500 cm^{-1} .

This investigation of $\text{LiYF}_4\cdot\text{Eu}^{3+}$ provides an extension of the energy identification. Location and assignments of 120 crystal-field levels are reported. These levels span the 0–39 000 cm^{-1} energy region and belong to 36 different SLJ multiplet manifolds of the $4f^6$ electronic configuration of Eu^{3+} . The data were obtained from optical absorption and fluorescence spectra at 298 K and 77 K. Crystal-field matrices are diagonalized both in D_{2d} and S_4 symmetry using a parametric Hamiltonian.

2. Experimental details

Crystals of LiYF_4 doped with Eu^{3+} were grown by spontaneous nucleation in the melt [4, 7]. The doping concentration is about 5 mol%. Samples were oriented by Laue photography and cut in such a way that the crystallographic c axis is perpendicular to two of the faces (for α spectra) or parallel (for σ and π spectra). The faces were optically polished. The crystal thickness and thus the optical path length was 1.5 mm. The fluorescence measurements are described elsewhere [4].

Optical absorption spectra were recorded using an AVIV 17DS spectrophotometer. In the visible and UV regions the instrument has a wavelength resolution better than 0.1 nm. In the

IR region the wavelength resolution is 0.3 nm. The wavelength accuracy is approximately ± 0.4 nm. Light polarization is achieved by a Glan-Thompson polarizer. For low-temperature measurements the sample is cooled in an optical Dewar (Oxford Instruments) filled with liquid nitrogen (77 K).

3. Structure and symmetry of the coordination polyhedron

The existence of LiYF_4 was first reported in 1961 by Thoma *et al* [8]. LiYF_4 crystallizes in the tetragonal scheelite (CaWO_4) structure, which belongs to space group C_{4h}^6 ($I4_1/a$) [9]. With respect to scheelite, in LiYF_4 , Y is at the Ca site, Li is at the W site and F is at the O site. Although Y^{3+} can be totally exchanged by Ln^{3+} ($\text{Ln}^{3+} = \text{Gd}^{3+} - \text{Lu}^{3+}$), Eu^{3+} can only partially substitute for Y^{3+} in single crystals. This is due to the difference in ionic radius between Eu^{3+} and Y^{3+} . Each Y^{3+} (or Eu^{3+}) is dodecahedrally surrounded by eight F^- ions. The point symmetry of such a dodecahedron is D_{2d} . In LiYF_4 the actual site symmetry at the rare-earth ion is not D_{2d} , but S_4 [10, 11]. This symmetry lowering is caused by a slight distortion of the dodecahedron. The distortion angle $\Delta\phi$ is 2.29° . As this angle is small, the D_{2d} symmetry remains a good approximation for the S_4 symmetry.

4. Spectroscopic assignments and selection rules

The crystal-field levels are assigned both in D_{2d} and S_4 symmetry (S_4 is a subgroup of D_{2d}). The irreducible representations are labelled according to the Koster notations [12]: $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$ and Γ_5 for D_{2d} , $\Gamma_1, \Gamma_2, \Gamma_3$ and Γ_4 for S_4 . As Γ_3 and Γ_4 are related in S_4 by time-reversal symmetry and degenerated in the absence of a magnetic field, they are designated $\Gamma_{3,4}$. A comparison between the irreducible representations of D_{2d} and S_4 , as well as the splitting of the J terms in those crystal fields, can be found in [12].

The assignments are based on the polarization characteristics of the transitions and the selection rules for electric dipole (ED) and magnetic dipole (MD) transitions (table 1). α , π and σ are defined in the usual manner: α spectrum, $c \parallel z$; π spectrum, $c \perp z$, $E \parallel c$; σ spectrum, $c \perp z$, $H \parallel c$, with z the propagation direction of the light and c the main crystal axis. E and H are the electric and magnetic field vectors of the incident light, respectively.

Table 1. Selection rules for induced ED and MD transitions in D_{2d} and S_4 symmetry.

D_{2d}	ED					MD				
	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
Γ_1	—	—	—	π	σ, α	—	σ	—	—	π, α
Γ_2	—	—	π	—	σ, α	σ	—	—	—	π, α
Γ_3	—	π	—	—	σ, α	—	—	—	σ	π, α
Γ_4	π	—	—	—	σ, α	—	—	σ	—	π, α
Γ_5	σ, α	σ, α	σ, α	σ, α	π	π, α	π, α	π, α	π, α	π, α

S_4	ED			MD		
	Γ_1	Γ_2	$\Gamma_{3,4}$	Γ_1	Γ_2	$\Gamma_{3,4}$
Γ_1	—	π	σ, α	σ	—	π, α
Γ_2	—	—	σ, α	—	σ	π, α
$\Gamma_{3,4}$	σ, α	σ, α	π	π, α	π, α	σ

5. Theoretical calculations

The energy levels of Eu^{3+} were analysed in terms of a parametric Hamiltonian [13, 14]:

$$H = H_0 + \sum_k F^k f_k + \zeta_{nl} A_{SO} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_i T^i t_i + \sum_k P^k p_k + \sum_k M^k m_k + H_{CF}. \quad (1)$$

H_0 involves the kinetic energy of the electrons and their interaction with the nucleus. It is the spherically symmetric one-electron part of the free-ion Hamiltonian and it shifts the energy of the entire $4f^N$ configuration ($N = 6$ for Eu^{3+}) alone. F^k ($k = 2, 4, 6$) are electron repulsion parameters and ζ_{nl} is the spin-orbit coupling constant. f_k and A_{SO} represent the angular parts of the electrostatic and spin-orbit interactions respectively. The parameters describing the two-body interaction are α , β and γ . $G(G_2)$ and $G(R_7)$ are the Casimir operators for the groups G_2 and R_7 , and L is the total orbital angular momentum. They represent effects that do not transform as the f_k . The three-particle configuration interaction is represented by $T^i t_i$ ($i = 2, 3, 4, 6, 7, 8$). T^i are the parameters and t_i the three-particle operators. Magnetically correlated corrections (spin-spin and spin-other-orbit relativistic corrections) are introduced by the Marvin integrals M^k ($k = 0, 2, 4$). The P^k parameters ($k = 2, 4, 6$) describe the two-body magnetic corrections (the most important is the electrostatically correlated spin-orbit perturbation). The free-ion part of the Hamiltonian incorporates 20 parameters.

The crystal-field part of the Hamiltonian (H_{CF}) is given in the formalism of Wybourne [15] by

$$H_{CF} = \sum_{i=0}^N \sum_{k=0}^{\infty} \sum_{q=-k}^k B_q^k C_q^k(i). \quad (2)$$

$C_q^k(i)$ is a spherical tensor of rank k , with components q . B_q^k are the crystal-field parameters. N is the number of electrons and i represents the i th electron. For f electrons $k \leq 6$. The expansion of the crystal-field Hamiltonian is symmetry dependent. According to the conventions of Koster [12], in which the x and y axes are parallel to the twofold C_2' -axes, H_{CF} is expanded in D_{2d} and S_4 as

$$H_{D_{2d}}^{\text{even}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4 (C_{-4}^4 + C_4^4) + B_0^6 C_0^6 + B_4^6 (C_{-4}^6 + C_4^6) \quad (3)$$

$$H_{S_4}^{\text{even}} = H_{D_{2d}}^{\text{even}} + iB_4^4 (C_{-4}^4 - C_4^4) + iB_4^6 (C_{-4}^6 - C_4^6). \quad (4)$$

Only the even terms have to be considered for the splitting of the levels under the crystal field, because the odd parts are zero within one configuration. If the σ_d mirror planes were chosen to be parallel to the x and y axes, the parameters B_4^4 and B_4^6 would have the opposite sign.

The two additional imaginary parameters iB_4^4 and iB_4^6 resulting from the slight distortion of the D_{2d} symmetry are not expected to be able to cause great energy shifts.

No axis rotation has been introduced to make one of the even k imaginary parameters (often iB_4^4) equal to zero. It was our opinion that in view of future intensity calculations it is more convenient to make one of the odd k imaginary parameters (iB_2^3) zero. Five crystal-field parameters have to be considered in D_{2d} and seven parameters in S_4 . In combination with the free-ion parameters, the total number of parameters is 25 for D_{2d} and 27 for S_4 .

Table 2. Assignments of the transitions in the polarized absorption spectra of $\text{LiYF}_4:\text{Eu}^{3+}$.

Energy (cm^{-1})	Transition	Polarization	Identification (D_{2d})	Identification (S_4)
3998	${}^7F_5 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
4050	${}^7F_5 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
4699	${}^7F_6 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_5^c \leftarrow \Gamma_2$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
4880	${}^7F_6 \leftarrow {}^7F_0$	π	$\Gamma_4^a \leftarrow \Gamma_1$	$\Gamma_2^a \leftarrow \Gamma_1$
4890	${}^7F_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
5076	${}^7F_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
16842	${}^5D_0 \leftarrow {}^7F_1$	σ	$\Gamma_1 \leftarrow \Gamma_2$	$\Gamma_1 \leftarrow \Gamma_1$
16934	${}^5D_0 \leftarrow {}^7F_1$	$\alpha + \pi$	$\Gamma_1 \leftarrow \Gamma_5$	$\Gamma_1 \leftarrow \Gamma_{3,4}$
18570	${}^5D_1 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_5 \leftarrow \Gamma_2$	$\Gamma_{3,4} \leftarrow \Gamma_1$
18676	${}^5D_1 \leftarrow {}^7F_1$	π	$\Gamma_5 \leftarrow \Gamma_5$	$\Gamma_{3,4} \leftarrow \Gamma_{3,4}$
18707	${}^5D_1 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_2 \leftarrow \Gamma_5$	$\Gamma_1 \leftarrow \Gamma_{3,4}$
19018	${}^5D_1 \leftarrow {}^7F_0$	$\alpha + \pi$	$\Gamma_5 \leftarrow \Gamma_1$	$\Gamma_{3,4} \leftarrow \Gamma_1$
19040	${}^5D_1 \leftarrow {}^7F_0$	σ	$\Gamma_2 \leftarrow \Gamma_1$	$\Gamma_1 \leftarrow \Gamma_1$
21070	${}^5D_2 \leftarrow {}^7F_1$	σ	$\Gamma_1 \leftarrow \Gamma_2$	$\Gamma_1 \leftarrow \Gamma_1$
21129	${}^5D_2 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_1 \leftarrow \Gamma_5$	$\Gamma_1 \leftarrow \Gamma_{3,4}$
21156	${}^5D_2 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_3 \leftarrow \Gamma_5$	$\Gamma_2^a \leftarrow \Gamma_{3,4}$
21176	${}^5D_2 \leftarrow {}^7F_1$	$\sigma + \pi$	$\Gamma_5 \leftarrow \Gamma_5$	$\Gamma_{3,4} \leftarrow \Gamma_{3,4}$
21207	${}^5D_2 \leftarrow {}^7F_1$	$\alpha + \pi$	$\Gamma_4 \leftarrow \Gamma_5$	$\Gamma_2^b \leftarrow \Gamma_{3,4}$
21444	${}^5D_2 \leftarrow {}^7F_0$	π	$\Gamma_3 \leftarrow \Gamma_1$	$\Gamma_2^a \leftarrow \Gamma_1$
21515	${}^5D_2 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5 \leftarrow \Gamma_1$	$\Gamma_{3,4} \leftarrow \Gamma_1$
21540	${}^5D_2 \leftarrow {}^7F_0$	π	$\Gamma_4 \leftarrow \Gamma_1$	$\Gamma_2^b \leftarrow \Gamma_1$
23921	${}^5D_3 \leftarrow {}^7F_1$	$\pi + \sigma + \alpha$	$\Gamma_3 \leftarrow \Gamma_2$	$\Gamma_2^a \leftarrow \Gamma_1$
23981	${}^5D_3 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_5^b \leftarrow \Gamma_2$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
23986	${}^5D_3 \leftarrow {}^7F_1$	π	$\Gamma_5^a \leftarrow \Gamma_5$	$\Gamma_{3,4}^a \leftarrow \Gamma_{3,4}$
24015	${}^5D_3 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_2 \leftarrow \Gamma_5$	$\Gamma_1 \leftarrow \Gamma_{3,4}$
24038	${}^5D_3 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_4 \leftarrow \Gamma_5$	$\Gamma_2^a \leftarrow \Gamma_{3,4}$
24077	${}^5D_3 \leftarrow {}^7F_1$	π	$\Gamma_5^b \leftarrow \Gamma_5$	$\Gamma_{3,4}^b \leftarrow \Gamma_{3,4}$
24500	${}^5L_6 \leftarrow {}^7F_1$	π	$\Gamma_3^a \leftarrow \Gamma_2$	$\Gamma_2^a \leftarrow \Gamma_1$
24513	${}^5L_6 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_5^a \leftarrow \Gamma_2$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
24596	${}^5L_6 \leftarrow {}^7F_1$	π	$\Gamma_5^a \leftarrow \Gamma_5$	$\Gamma_{3,4}^a \leftarrow \Gamma_{3,4}$
24597	${}^5L_6 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_3^a \leftarrow \Gamma_5$	$\Gamma_2^a \leftarrow \Gamma_{3,4}$
24937	${}^5L_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
24947	${}^5L_6 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_2 \leftarrow \Gamma_5$	$\Gamma_1^b \leftarrow \Gamma_{3,4}$
25078	${}^5L_6 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_1^b \leftarrow \Gamma_5$	$\Gamma_1^c \leftarrow \Gamma_{3,4}$
25225	${}^5L_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
25405	${}^5L_6 \leftarrow {}^7F_0$	π	$\Gamma_4^b \leftarrow \Gamma_1$	$\Gamma_2^d \leftarrow \Gamma_1$
25407	${}^5L_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
25985	${}^5G_3 \leftarrow {}^7F_1$	π	$\Gamma_3 \leftarrow \Gamma_2$	$\Gamma_2^a \leftarrow \Gamma_1$
25990	${}^5L_7 \leftarrow {}^7F_0$	π	$\Gamma_4^a \leftarrow \Gamma_1$	$\Gamma_2^a \leftarrow \Gamma_1$
25990	${}^5L_7 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
26050	${}^5L_7 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
26174	${}^5L_7 \leftarrow {}^7F_0$	π	$\Gamma_4^b \leftarrow \Gamma_1$	$\Gamma_2^c \leftarrow \Gamma_1$
26194	${}^5G_2 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5 \leftarrow \Gamma_1$	$\Gamma_{3,4} \leftarrow \Gamma_1$
26221	${}^5G_5 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_1^a \leftarrow \Gamma_5$	$\Gamma_1^a \leftarrow \Gamma_{3,4}$
26304	${}^5L_7 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
26373	${}^5L_7 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^d \leftarrow \Gamma_1$	$\Gamma_{3,4}^d \leftarrow \Gamma_1$
26395	${}^5G_6 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_3 \leftarrow \Gamma_2$	$\Gamma_2^d \leftarrow \Gamma_1$
26415	${}^5G_3 \leftarrow {}^7F_0$	π	$\Gamma_3 \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
26423	${}^5G_3 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_5^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$

Table 2. (continued)

Energy (cm^{-1})	Transition	Polarization	Identification (D_{2d})	Identification (S_4)
26531	${}^5G_3 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
26567	${}^5G_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
26598	${}^5G_5 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
26631	${}^5G_6 \leftarrow {}^7F_0$	π	$\Gamma_{44}^c \leftarrow \Gamma_1$	$\Gamma_2^b \leftarrow \Gamma_1$
26651	${}^5G_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
26734	${}^5G_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
26786	${}^5G_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
27183	${}^5L_8 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
27251	${}^5D_4 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_1^a \leftarrow \Gamma_5$	$\Gamma_1^a \leftarrow \Gamma_{3,4}$
27261	${}^5L_8 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
27264	${}^5D_4 \leftarrow {}^7F_1$	π	$\Gamma_{55}^b \leftarrow \Gamma_5$	$\Gamma_{3,4}^b \leftarrow \Gamma_{3,4}$
27290	${}^5D_4 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_2 \leftarrow \Gamma_5$	$\Gamma_1^b \leftarrow \Gamma_{3,4}$
27291	${}^5D_4 \leftarrow {}^7F_1$	π	$\Gamma_{55}^a \leftarrow \Gamma_5$	$\Gamma_{3,4}^a \leftarrow \Gamma_{3,4}$
27605	${}^5D_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
27630	${}^5D_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
27623	${}^5D_4 \leftarrow {}^7F_0$	π	$\Gamma_4 \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
27651	${}^5L_9 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
27682	${}^5L_9 \leftarrow {}^7F_0$	π	$\Gamma_{44}^a \leftarrow \Gamma_1$	$\Gamma_2^a \leftarrow \Gamma_1$
27789	${}^5L_9 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
28023	${}^5L_9 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
28411	${}^5L_{10} \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
30479	${}^5H_7 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_2^a \leftarrow \Gamma_5$	$\Gamma_1^a \leftarrow \Gamma_{3,4}$
30497	${}^5H_3 \leftarrow {}^7F_1$	π	$\Gamma_{55}^b \leftarrow \Gamma_5$	$\Gamma_{3,4}^b \leftarrow \Gamma_{3,4}$
30563	${}^5H_7 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_1 \leftarrow \Gamma_5$	$\Gamma_1^b \leftarrow \Gamma_{3,4}$
30564	${}^5H_7 \leftarrow {}^7F_1$	π	$\Gamma_{55}^b \leftarrow \Gamma_5$	$\Gamma_{3,4}^b \leftarrow \Gamma_{3,4}$
30659	${}^5H_7 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_{33}^b \leftarrow \Gamma_5$	$\Gamma_2^d \leftarrow \Gamma_{3,4}$
30898	${}^5H_7 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
30949	${}^5H_7 \leftarrow {}^7F_0$	π	$\Gamma_{44}^a \leftarrow \Gamma_1$	$\Gamma_2^c \leftarrow \Gamma_1$
31169	${}^5H_7 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^d \leftarrow \Gamma_1$	$\Gamma_{3,4}^d \leftarrow \Gamma_1$
31177	${}^5H_4 \leftarrow {}^7F_0$	π	$\Gamma_4 \leftarrow \Gamma_1$	$\Gamma_2^a \leftarrow \Gamma_1$
31261	${}^5H_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
31358	${}^5H_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
31403	${}^5H_5 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
31550	${}^5H_5 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
31608	${}^5H_6 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
32778	${}^5F_3 \leftarrow {}^7F_1$	π	$\Gamma_4 \leftarrow \Gamma_5$	$\Gamma_2^b \leftarrow \Gamma_{3,4}$
32936	${}^5F_1 \leftarrow {}^7F_1$	$\alpha + \sigma$	$\Gamma_2 \leftarrow \Gamma_5$	$\Gamma_1 \leftarrow \Gamma_{3,4}$
32967	${}^5F_1 \leftarrow {}^7F_1$	π	$\Gamma_5 \leftarrow \Gamma_5$	$\Gamma_{3,4} \leftarrow \Gamma_{3,4}$
33020	${}^5F_3 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
33102	${}^5F_3 \leftarrow {}^7F_0$	π	$\Gamma_4 \leftarrow \Gamma_1$	$\Gamma_2 \leftarrow \Gamma_1$
33512	${}^5F_4 \leftarrow {}^7F_0$	π	$\Gamma_4 \leftarrow \Gamma_1$	$\Gamma_2^a \leftarrow \Gamma_1$
33517	${}^5F_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
33563	${}^5F_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
33927	${}^5F_5 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$
33957	${}^5F_5 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^c \leftarrow \Gamma_1$	$\Gamma_{3,4}^c \leftarrow \Gamma_1$
33980	${}^5I_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^a \leftarrow \Gamma_1$	$\Gamma_{3,4}^a \leftarrow \Gamma_1$
34019	${}^5I_4 \leftarrow {}^7F_0$	$\alpha + \sigma$	$\Gamma_{55}^b \leftarrow \Gamma_1$	$\Gamma_{3,4}^b \leftarrow \Gamma_1$

Table 2. (continued)

Energy (cm ⁻¹)	Transition	Polarization	Identification (D _{2d})	Identification (S ₄)
34 252	⁵ I ₅ ← ⁷ F ₀	α + σ	Γ ₅ ^a ← Γ ₁	Γ _{3,4} ^a ← Γ ₁
34 793	⁵ I ₈ ← ⁷ F ₀	α + σ	Γ ₅ ^b ← Γ ₁	Γ _{3,4} ^b ← Γ ₁
34 829	⁵ I ₆ ← ⁷ F ₀	α + σ	Γ ₅ ^a ← Γ ₁	Γ _{3,4} ^a ← Γ ₁
34 865	⁵ I ₆ ← ⁷ F ₀	α + σ	Γ ₅ ^b ← Γ ₁	Γ _{3,4} ^b ← Γ ₁
34 877	⁵ I ₆ ← ⁷ F ₀	π	Γ ₅ ^a ← Γ ₁	Γ ₂ ^b ← Γ ₁
34 922	⁵ I ₈ ← ⁷ F ₀	α + σ	Γ ₅ ^c ← Γ ₁	Γ _{3,4} ^c ← Γ ₁
35 027	⁵ I ₆ ← ⁷ F ₀	π	Γ ₃ ^b ← Γ ₁	Γ ₂ ^d ← Γ ₁
36 113	⁵ K ₅ ← ⁷ F ₀	α + σ	Γ ₅ ^b ← Γ ₁	Γ _{3,4} ^b ← Γ ₁
37 283	⁵ K ₆ ← ⁷ F ₀	α + σ	Γ ₅ ^b ← Γ ₁	Γ _{3,4} ^b ← Γ ₁
37 327	⁵ K ₆ ← ⁷ F ₀	π	Γ ₄ ← Γ ₁	Γ ₂ ^d ← Γ ₁
37 355	⁵ K ₆ ← ⁷ F ₀	α + σ	Γ ₅ ^c ← Γ ₁	Γ _{3,4} ^c ← Γ ₁
38 209	⁵ K ₇ ← ⁷ F ₀	α + σ	Γ ₅ ^c ← Γ ₁	Γ _{3,4} ^c ← Γ ₁
38 216	⁵ K ₇ ← ⁷ F ₀	π	Γ ₄ ← Γ ₁	Γ ₂ ← Γ ₁
38 267	⁵ K ₇ ← ⁷ F ₀	α + σ	Γ ₅ ^d ← Γ ₁	Γ _{3,4} ^d ← Γ ₁
38 558	⁵ K ₈ ← ⁷ F ₀	α + σ	Γ ₅ ^a ← Γ ₁	Γ _{3,4} ^a ← Γ ₁
38 559	⁵ K ₈ ← ⁷ F ₀	π	Γ ₃ ← Γ ₁	Γ ₂ ← Γ ₁

Calculated values of the crystal-field levels are found by diagonalizing the matrix formed by the action of the total Hamiltonian on the unperturbed wavefunctions.

Due to the degeneracy of the 4f⁶ configuration (3003), a 3003 × 3003 matrix has to be diagonalized. Fortunately the complete crystal-field matrix can be split into four submatrices, corresponding to four crystal quantum numbers (μ = 0, ±1, 2). The dimensions of these matrices are further reduced to about 260 by truncating all energy levels above 50 000 cm⁻¹. Because no experimental data above 40 000 cm⁻¹ were available, it was necessary to assume that the truncated levels do not have an appreciable influence on the underlying levels. The starting parameters are optimized in a least-squares fit to a set of experimentally determined energy levels. The root mean square deviation σ between the experimental and calculated energy level values was used as a figure of merit to describe the quality of a fit.

$$\sigma = \sqrt{\sum (E_{\text{exp}} - E_{\text{calc}})^2 / (N - P)} \quad (5)$$

where E_{exp} is the experimental energy value, E_{calc} the calculated energy, N the number of levels that was used in the fit and P the number of variable parameters.

6. Experimental results

The absorption spectra were recorded at 298 K and 77 K in the spectral interval 3900–39 000 cm⁻¹ (figures 1–3). The lines are not much broader at room temperature than at 77 K, but they are weaker due to the depopulation of the ground state. At 77 K only the ⁷F₀ level is populated. At room temperature, transitions can also take place from the ⁷F₁ level, so additional lines are expected. No transitions from the ⁷F₂ level were observed. Eu³⁺ has the advantage that the ⁷F₀ ground state is not degenerate. This considerably simplifies the interpretation of the spectrum.

120 crystal-field levels were located and assigned, spanning 36 different *SLJ* multiplets. Since the crystal-field structure in the spectral region above 26 000 cm⁻¹ is rather congested,

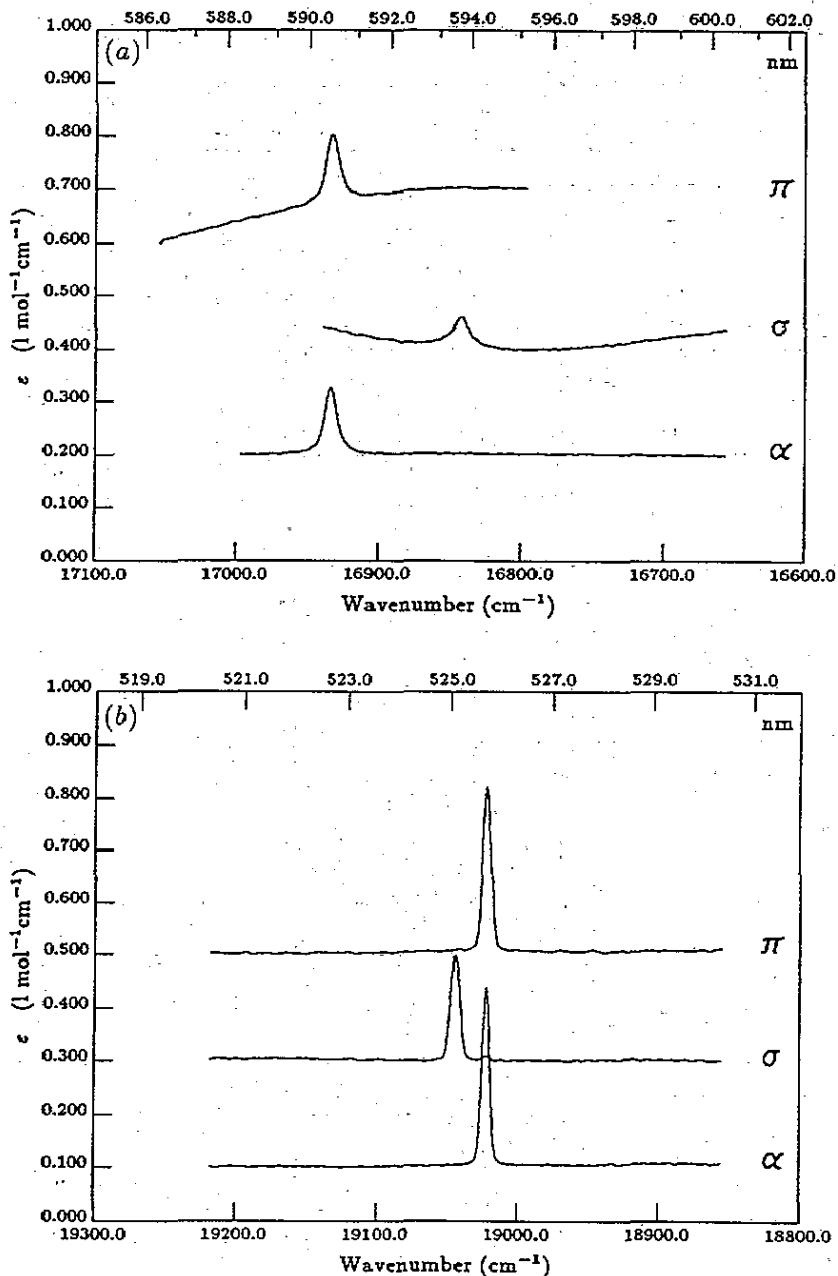


Figure 1. Polarized absorption spectra at room temperature of the MD transitions (a) ${}^5\text{D}_0 \leftarrow {}^7\text{F}_1$ and (b) ${}^5\text{D}_1 \leftarrow {}^7\text{F}_0$.

initial assignments were limited to well isolated groups. After the first calculations progressively more levels could be assigned. Mainly in the 26 000–27 800 cm^{-1} and in the 30 000–35 000 cm^{-1} regions the manifolds of the different SLJ terms overlap and it is difficult to assign a single SLJ label to the levels, because of a strong violation of the Russell–Saunders coupling scheme. Not all calculated levels were observed because of low transition probabilities. Since for the higher wavenumbers only a few levels within an SLJ

Table 3. Calculated and observed energy levels (cm^{-1}) in $\text{LiYF}_4:\text{Eu}^{3+}$ with assignments in D_{2d} and S_4 symmetry.

SLJ	E_{exp}	E_{calc} (D_{2d})	Irrep. D_{2d}	E_{calc} (S_4)	Irrep. S_4
7F_0	0	0	Γ_1	0	Γ_1
7F_1	334	341	Γ_5	341	$\Gamma_{3,4}$
7F_1	430	432	Γ_2	432	Γ_1
7F_2	891	868	Γ_4	869	Γ_2^a
7F_2	976	965	Γ_5	964	$\Gamma_{3,4}$
7F_2	1150	1164	Γ_3	1164	Γ_2^b
7F_2	1172	1176	Γ_1	1179	Γ_1
7F_3	1859	1846	Γ_4	1845	Γ_2^a
7F_3	1873	1858	Γ_5^a	1858	$\Gamma_{3,4}^a$
7F_3	1903	1881	Γ_2	1882	Γ_1
7F_3	1951	1950	Γ_5^b	1950	$\Gamma_{3,4}^b$
7F_3	2038	2032	Γ_3	2033	Γ_2^b
7F_4	2606	2590	Γ_1^a	2588	Γ_1^a
7F_4	2812	2787	Γ_5^a	2789	$\Gamma_{3,4}^a$
7F_4	2870	2865	Γ_2	2863	Γ_1^b
7F_4	2905	2873	Γ_3	2874	Γ_2^a
7F_4	2978	2966	Γ_4	2972	Γ_2^b
7F_4	3013	3010	Γ_5^b	3011	$\Gamma_{3,4}^b$
7F_4	—	3062	Γ_1^b	3061	Γ_1^c
7F_5	3795	3765	Γ_4	3766	Γ_2^a
7F_5	3807	3778	Γ_5^a	3779	$\Gamma_{3,4}^a$
7F_5	—	3821	Γ_2^a	3822	Γ_1^a
7F_5	3998	3983	Γ_5^b	3983	$\Gamma_{3,4}^b$
7F_5	4008	3992	Γ_1	3996	Γ_1^b
7F_5	—	3993	Γ_2^b	3998	Γ_1^c
7F_5	4050	4047	Γ_5^c	4050	$\Gamma_{3,4}^c$
7F_5	4070	4069	Γ_3	4069	Γ_2^b
7F_6	4877	4873	Γ_4^a	4877	Γ_2^a
7F_6	4890	4881	Γ_5^a	4884	$\Gamma_{3,4}^a$
7F_6	4891	4889	Γ_1^a	4892	Γ_1^a
7F_6	—	5031	Γ_2	5030	Γ_1^b
7F_6	5076	5070	Γ_5^b	5071	$\Gamma_{3,4}^b$
7F_6	—	5109	Γ_3^a	5110	Γ_2^b
7F_6	—	5118	Γ_1^b	5119	Γ_1^c
7F_6	5129	5123	Γ_5^c	5124	$\Gamma_{3,4}^c$
7F_6	5200	5194	Γ_4^b	5198	Γ_2^c
7F_6	—	5195	Γ_3^b	5199	Γ_2^d
5D_0	17270	17289	Γ_1	17289	Γ_1
5D_1	19018	19010	Γ_5	19011	$\Gamma_{3,4}$
5D_1	19040	19044	Γ_2	19045	Γ_1

Table 3. (continued)

SLJ	E_{exp}	E_{calc} (D_{2d})	Irrep. D_{2d}	E_{calc} (S_4)	Irrep. S_4
5D_2	21454	21438	Γ_3	21439	Γ_2^a
5D_2	21490	21468	Γ_1	21468	Γ_1
5D_2	21512	21497	Γ_5	21479	$\Gamma_{3,4}$
5D_2	21540	21508	Γ_4	21508	Γ_2^b
5D_3	24320	24338	Γ_5^a	24338	$\Gamma_{3,4}^a$
5D_3	24349	24348	Γ_2	24349	Γ_1
5D_3	24351	24351	Γ_3	24349	Γ_2^a
5D_3	24372	24352	Γ_4	24355	Γ_2^b
5D_3	24411	24382	Γ_5^b	24388	$\Gamma_{3,4}^b$
5L_6	24930	24925	Γ_3^a	24925	Γ_2^a
5L_6	24937	24940	Γ_5^a	24940	$\Gamma_{3,4}^a$
5L_6	—	24953	Γ_1^a	24953	Γ_1^a
5L_6	—	25049	Γ_4^a	25045	Γ_2^b
5L_6	25060	25050	Γ_3^b	25046	Γ_2^c
5L_6	25225	25223	Γ_5^b	25226	$\Gamma_{3,4}^b$
5L_6	25281	25272	Γ_2	25275	Γ_1^b
5L_6	25405	25372	Γ_4^b	25370	Γ_2^d
5L_6	25407	25373	Γ_5^c	25372	$\Gamma_{3,4}^c$
5L_6	25412	25382	Γ_1^b	25382	Γ_1^c
5L_7	25990	25985	Γ_4^a	25986	Γ_2^a
5L_7	—	25988	Γ_2^a	25987	Γ_1^a
5L_7	25990	25989	Γ_5^a	25988	$\Gamma_{3,4}^a$
5L_7	—	25994	Γ_1^a	25992	Γ_1^b
5L_7	26050	26069	Γ_5^b	26066	$\Gamma_{3,4}^b$
5G_2	—	26136	Γ_1	26137	Γ_1
5L_7	—	26167	Γ_3^a	26165	Γ_2^b
5L_7	26174	26182	Γ_4^b	26179	Γ_2^c
5G_2	26194	26203	Γ_5	26204	$\Gamma_{3,4}$
5L_7	26304	26293	Γ_5^c	26292	$\Gamma_{3,4}^c$
5L_7	—	26303	Γ_3^b	26304	Γ_2^d
5L_7	—	26316	Γ_2^b	26314	Γ_1^c
5L_7	26373	26356	Γ_5^d	26358	$\Gamma_{3,4}^d$
5G_2	—	26364	Γ_4	26366	Γ_2^e
5G_2	—	26393	Γ_3	26396	Γ_2^b
5G_3	26415	26397	Γ_3	26397	Γ_2^a
5G_3	26423	26405	Γ_5^a	26407	$\Gamma_{3,4}^a$
5G_3	—	26448	Γ_4	26450	Γ_2^b
5G_3	—	26458	Γ_2	26457	Γ_1
5G_5	—	26482	Γ_4	26485	Γ_2^a
5G_4	—	26498	Γ_1^a	26499	Γ_1^a
5G_5	—	26503	Γ_5^a	26500	$\Gamma_{3,4}^a$
5G_6	—	26511	Γ_4^a	26512	Γ_2^a
5G_3	26531	26518	Γ_5^b	26518	$\Gamma_{3,4}^b$
5G_4	—	26527	Γ_1^b	26523	Γ_1^b
5G_6	—	26544	Γ_2^a	26546	Γ_1^a

Table 3. (continued)

SLJ	E_{exp}	E_{calc} (D_{2d})	Irrep. D_{2d}	E_{calc} (S_4)	Irrep. S_4
5G_4	—	26547	Γ_5^a	26547	$\Gamma_{3,4}$
5G_4	—	26562	Γ_3	26561	Γ_2^b
5G_5	26555	26563	Γ_1^a	26563	Γ_1^a
5G_6	26567	26566	Γ_5^a	26566	$\Gamma_{3,4}^a$
5G_6	—	26599	Γ_1^a	26603	Γ_1^a
5G_6	—	26616	Γ_4^b	26615	Γ_2^a
5G_5	26598	26623	Γ_5^b	26624	$\Gamma_{3,4}^b$
5G_6	26631	26635	Γ_4^c	26639	Γ_2^b
5G_6	26651	26659	Γ_5^b	26658	$\Gamma_{3,4}^b$
5G_4	—	26665	Γ_1^b	26664	Γ_1^c
5G_5	—	26685	Γ_2^a	26685	Γ_1^b
5G_6	—	26693	Γ_3	26691	Γ_2^c
5G_4	—	26694	Γ_4	26696	Γ_2^b
5G_6	26729	26702	Γ_3	26705	Γ_2^d
5G_5	—	26709	Γ_5^c	26710	$\Gamma_{3,4}^d$
5G_5	—	26733	Γ_1^b	26733	Γ_1^c
5G_6	26734	26752	Γ_5^c	26753	$\Gamma_{3,4}^c$
5G_5	—	26764	Γ_3	26766	Γ_2^b
5G_5	—	26774	Γ_2^b	26774	Γ_1^c
5G_4	26786	26776	Γ_5^b	26780	$\Gamma_{3,4}^b$
5L_8	—	26978–27329	—	26980–27331	—
5D_4	27585	27580	Γ_1^a	27582	Γ_1^a
5D_4	27601	27595	Γ_5^a	27596	$\Gamma_{3,4}^a$
5D_4	—	27611	Γ_3	27611	Γ_2^a
5D_4	27623	27617	Γ_4	27617	Γ_2^b
5D_4	27624	27624	Γ_2	27626	Γ_1^b
5D_4	27627	27627	Γ_5^b	27629	$\Gamma_{3,4}^b$
5D_4	—	27650	Γ_1^b	27651	Γ_1^c
5L_9	—	27663–28090	—	27665–28088	—
${}^5L_{10}$	—	28102–28671	—	28108–28670	—
5H_3	—	30645	Γ_3	30644	Γ_2^a
5H_3	—	30696	Γ_5^a	30698	$\Gamma_{3,4}^a$
5H_3	—	30758	Γ_2^a	30760	Γ_1
5H_7	—	30785	Γ_4^a	30782	Γ_2^b
5H_7	30813	30803	Γ_2^a	30805	Γ_1^a
5H_7	—	30807	Γ_5^a	30809	$\Gamma_{3,4}^a$
5H_7	—	30829	Γ_3^a	30833	Γ_2^a
5H_3	30831	30852	Γ_5^b	30853	$\Gamma_{3,4}^b$
5H_7	30897	30896	Γ_1	30896	Γ_1^b
5H_7	30898	30910	Γ_5^b	30909	$\Gamma_{3,4}^b$
5H_7	30949	30936	Γ_4^b	30936	Γ_2^b
5H_7	30993	30958	Γ_3^b	30956	Γ_2^c
5H_4	—	31040	Γ_5^c	31044	$\Gamma_{3,4}^c$
5H_4	—	31123	Γ_5^b	31124	$\Gamma_{3,4}^a$
5H_4	—	31133	Γ_1^a	31133	Γ_1^a

Table 3. (continued)

SLJ	E_{exp}	E_{calc} (D_{2d})	Irrep. D_{2d}	E_{calc} (S_4)	Irrep. S_4
$^5\text{H}_7$	—	31 141	Γ_4^b	31 141	Γ_2^d
$^5\text{H}_7$	—	31 141	Γ_2^b	31 144	Γ_1^c
$^5\text{H}_7$	31 169	31 179	Γ_5^d	31 181	$\Gamma_{3,4}^d$
$^5\text{H}_4$	31 177	31 194	Γ_4	31 195	Γ_2^a
$^5\text{H}_4$	—	31 229	Γ_2	31 228	Γ_1^b
$^5\text{H}_4$	—	31 229	Γ_3	31 230	Γ_2^b
$^5\text{H}_4$	31 261	31 233	Γ_5^b	31 233	$\Gamma_{3,4}^b$
$^5\text{H}_4$	—	31 249	Γ_1^b	31 249	Γ_1^c
$^5\text{H}_5$	—	31 322	Γ_5^a	31 323	$\Gamma_{3,4}^a$
$^5\text{H}_5$	—	31 329	Γ_3	31 331	Γ_2^a
$^5\text{H}_5$	—	31 336	Γ_2^a	31 335	Γ_1^a
$^5\text{H}_6$	—	31 348	Γ_1	31 351	Γ_1^a
$^5\text{H}_6$	31 358	31 351	Γ_5^a	31 352	$\Gamma_{3,4}^a$
$^5\text{H}_6$	—	31 362	Γ_4^a	31 364	Γ_2^a
$^5\text{H}_5$	31 403	31 400	Γ_5^b	31 400	$\Gamma_{3,4}^b$
$^5\text{H}_6$	—	31 422	Γ_2	31 422	Γ_1^b
$^5\text{H}_5$	—	31 423	Γ_1	31 423	Γ_1^b
$^5\text{H}_6$	—	31 439	Γ_4^b	31 440	Γ_2^b
$^5\text{H}_6$	—	31 489	Γ_5^b	31 490	$\Gamma_{3,4}^b$
$^5\text{H}_6$	—	31 499	Γ_3	31 501	Γ_2^c
$^5\text{H}_5$	31 550	31 553	Γ_5^c	31 555	$\Gamma_{3,4}^c$
$^5\text{H}_6$	—	31 570	Γ_3	31 571	Γ_2^d
$^5\text{H}_5$	—	31 583	Γ_2^b	31 584	Γ_1^c
$^5\text{H}_5$	—	31 590	Γ_4	31 592	Γ_2^b
$^5\text{H}_6$	—	31 606	Γ_1	31 608	Γ_1^c
$^5\text{H}_6$	31 608	31 607	Γ_5^c	31 608	$\Gamma_{3,4}^c$
$^5\text{F}_3$	—	32 875	Γ_3	32 874	Γ_2^a
$^3\text{F}_0$	—	32 886	Γ_1	32 889	Γ_1
$^5\text{F}_2$	—	32 896	Γ_4	32 897	Γ_2^a
$^5\text{F}_2$	—	32 942	Γ_5	32 942	$\Gamma_{3,4}^a$
$^5\text{F}_3$	—	33 005	Γ_5^a	33 004	$\Gamma_{3,4}^a$
$^5\text{F}_2$	—	33 009	Γ_1	33 011	Γ_1
$^5\text{F}_2$	—	33 023	Γ_3	33 023	Γ_2^b
$^5\text{F}_3$	33 020	33 028	Γ_5^b	33 033	$\Gamma_{3,4}^b$
$^5\text{F}_3$	—	33 040	Γ_2	33 041	Γ_1
$^5\text{F}_3$	33 102	33 117	Γ_4	33 118	Γ_2^b
$^5\text{F}_1$	33 270	33 274	Γ_2	33 275	Γ_1
$^5\text{F}_1$	33 301	33 279	Γ_5	33 280	$\Gamma_{3,4}$
$^5\text{F}_4$	—	33 378	Γ_1^a	33 378	Γ_1^a
$^5\text{F}_4$	33 512	33 418	Γ_4	33 419	Γ_2^a
$^5\text{F}_4$	33 517	33 426	Γ_5^a	33 428	$\Gamma_{3,4}^a$
$^5\text{F}_4$	—	33 433	Γ_2	33 434	Γ_1^b
$^5\text{F}_4$	—	33 457	Γ_3	33 460	Γ_2^b
$^5\text{F}_4$	33 563	33 470	Γ_5^b	33 471	$\Gamma_{3,4}^b$
$^5\text{F}_4$	—	33 490	Γ_1^b	33 491	Γ_1^c

Table 3. (continued)

<i>SLJ</i>	E_{exp}	E_{calc} (D_{2d})	Irrep. D_{2d}	E_{calc} (S_4)	Irrep. S_4
5I_4	—	33 861	Γ_1^a	33 860	Γ_1^a
5F_5	—	33 886	Γ_2^a	33 886	Γ_1^a
5F_5	—	33 896	Γ_5^a	33 896	$\Gamma_{3,4}^a$
5F_5	—	33 897	Γ_4	33 897	Γ_2^a
5I_4	—	33 898	Γ_3	33 897	Γ_2^a
5F_5	33 927	33 919	Γ_5^b	33 920	$\Gamma_{3,4}^b$
5F_5	—	33 933	Γ_1	33 934	Γ_1^b
5F_5	—	33 935	Γ_3	33 935	Γ_2^b
5F_5	—	33 942	Γ_2^b	33 944	Γ_1^c
5F_5	33 957	33 944	Γ_5^c	33 945	$\Gamma_{3,4}^c$
5I_4	33 980	33 967	Γ_5^a	33 968	$\Gamma_{3,4}^a$
5I_4	—	33 992	Γ_2	33 992	Γ_1^b
5I_4	34 019	34 009	Γ_5^b	34 011	$\Gamma_{3,4}^b$
5I_4	—	34 047	Γ_4	34 047	Γ_2^b
5I_4	—	34 081	Γ_1^b	34 084	Γ_1^c
5I_5	—	34 203–34 451	—	34 204–34 452	—
5I_8	—	34 733	Γ_4^a	34 733	Γ_2^a
5I_8	—	34 740	Γ_5^a	34 740	$\Gamma_{3,4}^a$
5I_6	—	34 742	Γ_1^a	34 743	Γ_1^a
5I_8	—	34 754	Γ_3^a	34 755	Γ_2^a
5I_8	34 793	34 775	Γ_5^b	34 776	$\Gamma_{3,4}^b$
5I_6	34 829	34 787	Γ_5^a	34 787	$\Gamma_{3,4}^a$
5I_8	—	34 787	Γ_2^a	34 787	Γ_1^a
5I_8	—	34 797	Γ_1^a	34 799	Γ_1^b
5I_6	—	34 803	Γ_4^a	34 805	Γ_2^a
5I_6	—	34 856	Γ_2^a	34 854	Γ_1^b
5I_6	34 865	34 858	Γ_5^b	34 958	$\Gamma_{3,4}^b$
5I_8	—	34 902	Γ_1^b	34 906	Γ_1^c
5I_6	34 877	34 905	Γ_3^a	34 906	Γ_2^b
5I_8	—	34 936	Γ_1^b	34 937	Γ_1^d
5I_8	34 922	34 939	Γ_5^c	34 940	$\Gamma_{3,4}^c$
5I_8	—	34 958	Γ_4^b	34 957	Γ_2^c
5I_6	—	34 976	Γ_3^b	34 978	Γ_2^c
5I_8	—	34 976	Γ_4^c	34 982	Γ_2^d
5I_8	—	34 979	Γ_5^d	34 982	$\Gamma_{3,4}^d$
5I_8	—	34 997	Γ_1^c	34 999	Γ_1^a
5I_6	35 027	35 012	Γ_3^b	35 013	Γ_2^d
5I_6	—	35 014	Γ_5^c	35 015	$\Gamma_{3,4}^c$
5I_6	—	35 026	Γ_1^b	35 027	Γ_1^c
5I_7	—	35 219–35 506	—	35 221–35 507	—
5K_5	—	36 007–36 239	—	36 007–36 239	—
5K_6	—	37 154–37 353	—	37 154–37 354	—
5K_7 - 3P_1	—	38 072–38 249	—	38 073–38 250	—
5G_2	—	38 462–38 490	—	38 462–38 490	—
5K_8	—	38 553–38 662	—	38 556–38 662	—

multiplet were observed, it was not possible to determine their barycentres. Some additional

Table 4. Energy parameters (in cm^{-1}) for the $4f^6$ electronic configuration of $\text{LiYF}_4:\text{Eu}^{3+}$ in D_{2d} and S_4 symmetry.

Parameter	D_{2d}	S_4
F^2		82210 ± 9
F^4		59154 ± 19
F^6		43090 ± 11
α		21 ± 1
β		-554 ± 10
γ		1326 ± 8
T^2		370 ± 3
T^3		(40)
T^4		(40)
T^6		-300 ± 28
T^7		(370)
T^8		(370)
ζ		1330 ± 1
M^0		2.416 ± 0.046
M^2		1.353
M^4		0.918
P^2		307 ± 10
P^4		229
P^6		153
B_0^2	349 ± 23	348 ± 23
B_0^4	-749 ± 32	-775 ± 32
B_0^6	-93 ± 46	-80 ± 46
B_4^4	-1054 ± 22	-1045 ± 21
B_4^6	-778 ± 29	-772 ± 31
iB_4^4		25 ± 20
iB_4^6		180 ± 40

peaks in the spectra turned out to be caused by holmium impurities in $\text{LiYF}_4:\text{Eu}^{3+}$. In the UV region the Eu^{3+} peaks are superimposed on a broad oscillating background signal. The transitions observed are given in table 2. They are labelled according to the largest SLJ components. When a peak was found at both temperatures or in different polarizations at slightly shifted wavenumbers, an average value is reported. Thus contingent temperature dependence of the lines due to a changing of the crystal field by thermal expansion or contraction of the crystal lattice is neglected.

Most transitions are predominantly ED in character. This is also evident from the nearly identical α and σ polarized spectra. A few transitions occur by a nearly pure MD mechanism, e.g. ${}^5D_1 \leftarrow {}^7F_0$, ${}^5D_1 \leftarrow {}^7F_1$, ${}^5D_2 \leftarrow {}^7F_1$ and ${}^5F_1 \leftarrow {}^7F_1$. All transitions from the Γ_1 ground state to Γ_3 (D_{2d} labelling) have a low intensity. Such transitions are allowed in S_4 , but not by the selection rules in D_{2d} symmetry. Spectral transitions with $\Delta J \neq 0, 1, 2, 4, 6$ are forbidden both by MD and by induced-ED selection rules. Due to J mixing these transitions become allowed but they have very low transition probabilities. This partly explains why in the higher-energy regions few levels are found experimentally in comparison to the large number expected theoretically. It follows from the selection rules that experimental evidence for Γ_1 , Γ_2 and Γ_3 levels (in D_{2d}) can only be acquired from transitions starting from the 7F_1 level. Most observed levels belong therefore to the Γ_4 and Γ_5 irreducible representations.

The parameters in [4], which were calculated with a strongly reduced basis of the 49 7F crystal-field levels, cannot accurately describe the wavefunctions of levels higher than 5D_1 .

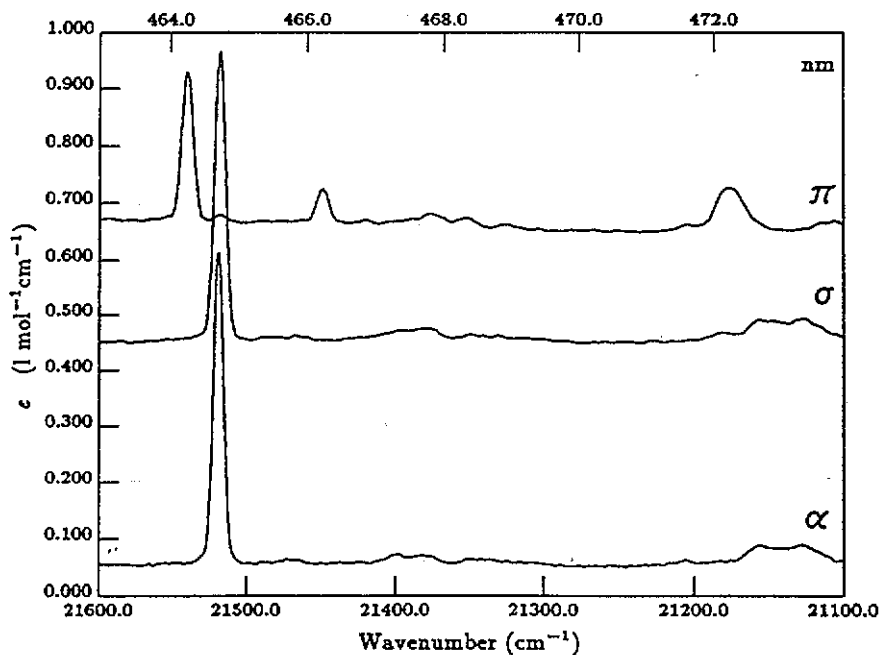


Figure 2. ${}^5D_2 \leftarrow {}^7F_{0,1}$ absorption in $\text{LiYF}_4:\text{Eu}^{3+}$ at room temperature.

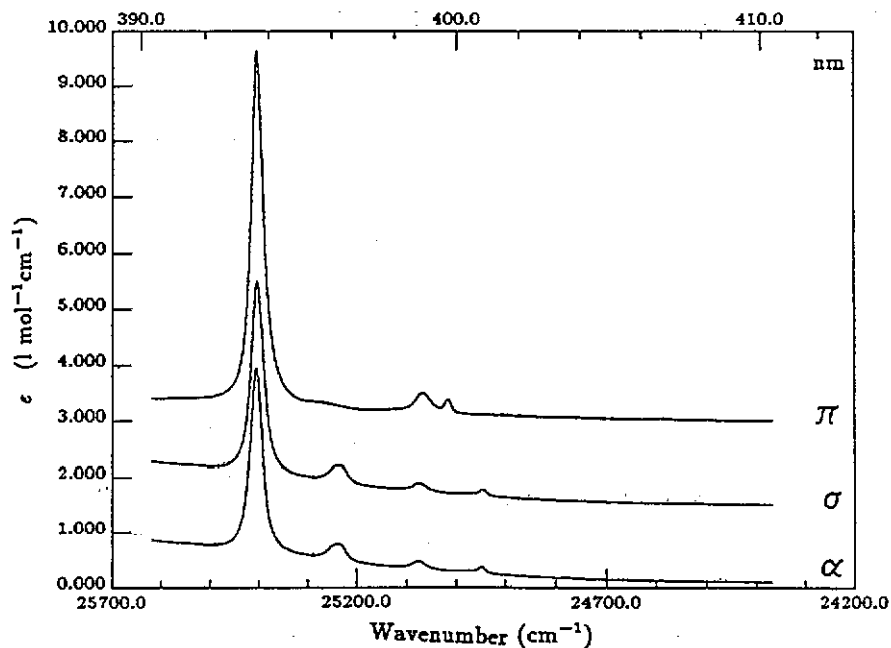


Figure 3. Polarized absorption spectra of ${}^5L_6 \leftarrow {}^7F_{0,1}$ in $\text{LiYF}_4:\text{Eu}^{3+}$ at room temperature.

The standard deviations σ of our present fit of calculated against experimental energy levels is $\sim 14 \text{ cm}^{-1}$. The number of available experimental barycentres was insufficient to vary all free-ion parameters independently. The repulsion parameters are difficult to determine

accurately because most observed levels lie within F and D multiplets. Starting parameters for the free ion were chosen from Eu^{3+} in another host crystal (EuODA) [16]; the starting crystal-field parameters came from [4]. J -mixing effects have been taken into account. The P^k and M^k values were constrained according to the relationships $P^4/P^2 = 0.75$, $P^6/P^2 = 0.5$, $M^2/M^0 = 0.56$ and $M^4/M^0 = 0.38$. Finally, the crystal-field parameters were determined (D_{2d} and S_4). For the S_4 calculations the free-ion parameters of D_{2d} were retained, since the S_4 distortion is small. Moreover a variation of the free-ion parameters for S_4 did not result in a better fit.

The calculated and observed energy levels are listed in table 3. Not all levels calculated in the high-energy range are given, because this would make the table too lengthy (more than 300 levels were calculated for Eu^{3+} in the 0–39 000 cm^{-1} spectral region). The agreement between theory and experiment is in general fairly good. A great discrepancy, however, was found for the transitions to ${}^5\text{F}_4$. These levels were excluded from the fit. A distinction (in D_{2d}) between the irreducible representations Γ_1 and Γ_2 on one hand and between Γ_3 and Γ_4 on the other hand was based on the symmetry of the largest components of the wavefunctions.

The D_{2d} and S_4 parameters are given in table 4. The splitting of the crystal-field levels is rather insensitive to a variation of the imaginary crystal-field parameters in S_4 .

7. Conclusions

The polarized absorption spectra of $\text{LiYF}_4:\text{Eu}^{3+}$ were investigated in the near IR, the visible and the UV spectral regions (3900–39 000 cm^{-1}) at 298 K and at 77 K. In combination with earlier published fluorescence results [4] a wide range of the $4f^6$ electronic configurations of Eu^{3+} could be calculated. Assignments were made in D_{2d} and S_4 symmetry. It has been shown that the actual S_4 symmetry is fairly well approximated by the D_{2d} symmetry.

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References

- [1] Shand W A 1969 *J. Cryst. Growth* 5 143
- [2] Morrison A and Leavitt R P 1982 *Handbook on the Physics and Chemistry of Rare Earths* vol 5 (Amsterdam: Elsevier) p 625
- [3] Jayasankar C K, Reid M F and Richardson F S 1989 *Phys. Status Solidi* b 155 559
- [4] Görller-Walrand C, Behets M, Porcher P, Moune-Mini O K and Laursen I 1985 *Inorg. Chim. Acta* 109 83
- [5] Görller-Walrand C, Behets M, Porcher P and Carnall W T 1986 *J. Less-Common. Met.* 126 271
- [6] Bihari B, Sharma K K and Erickson L E 1990 *J. Phys.: Condens. Matter* 2 5703
- [7] Laursen I and Holmes H 1974 *J. Phys. C: Solid State Phys.* 7 3765
- [8] Thoma R E, Weaver C F, Friedman H A, Insley H, Harris L A and Yakel H A 1961 *J. Phys. Chem.* 65 1096
- [9] Wyckoff R W G 1960 *Crystal Structures* vol III (New York: Interscience)
- [10] Vishwamittar and Purri S P 1974 *J. Phys. C: Solid State Phys.* 7 1337

- [11] Umland W 1981 *Chem. Phys. Lett.* **77** 58
- [12] Koster G F, Dimmock J O, Wheeler R G and Statz H 1963 *Properties of the Thirty-Two Point Groups* (Cambridge, MA: MIT Press)
- [13] Crosswhite H M and Crosswhite H 1984 *J. Opt. Soc. Am.* B **1** 246
- [14] Carnall W T, Goodman G L, Rajnak K and Rana R S 1989 *J. Chem. Phys.* **90** 3443
- [15] Wybourne B G 1965 *Spectroscopic Properties of Rare Earths* (New York: Interscience)
- [16] Berry M T, Schwieters C and Richardson F 1988 *Chem. Phys.* **122** 105