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f–f Transition intensities of europium(III) acetate complexes in a single crystal and in solution

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Abstract

Optical absorption spectra of Eu^{III}-acetate complexes in a single crystal and in solution as well as of the Eu^{III}-aquoion were analyzed. With decreasing temperature from 293 to 4 K an unusually strong intensity decrease of the $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_0$ transitions in the crystal was detected. A distinct influence of light polarization on these transitions caused by crystal anisotropy was observed. Spectral intensities of the investigated systems were parametrized in terms of the Judd–Ofelt theory.

Keywords: Absorption; Intensity analysis; Lanthanide; Europium; Acetate

1. Introduction

Complexes of lanthanide acetates have been investigated by electronic spectroscopy methods both in solution [1–5] and crystals [6–9]. The use of these techniques has revealed that only a significant excess of the ligand in the buffered solution does not cause further changes in the observed f–f electronic spectra. Contrary to crystals of lanthanide complexes with acetic acid derivatives [10–15], all the crystals of lanthanide acetates examined so far are characterized by relatively high intensities of the hypersensitive transitions at room temperature, which corresponds well with the relevant intensities of the appropriate complexes in solution [7–9]. With a decrease of temperature to 4 K, one may observe, however, a very strong intensity loss of the hypersensitive transitions in acetate crystals. Most probably, the hypersensitive $^7F_0 \rightarrow {}^5D_2$ transition of the Eu^{III} ion should be detected for all acetate complexes with different Ln^{III} ions, the most sensitive to changes of the metal ion environment. For this transition, only the $U^{(2)}$ matrix element has a non-zero value [16]. Thus far, spectroscopic studies of Eu^{III}-acetate have been limited to luminescence [2], NMR [17], IR and Raman studies [18]. The aim of this paper is to report a detailed analysis of the Eu^{III}-acetate electronic absorption spectra both in the single crystal and in solution. We expect that such an analysis will enable us to find a correlation between the spectral properties of the complex species in solution and that of a well-defined species in the crystal.

2. Experimental

Crystals of europium acetate were prepared by a method described previously [7] and checked by X-ray diffraction, which revealed that they were isomorphic with the centrosymmetric, dimeric $[Gd_2(CH_3COO)_6 \cdot 4H_2O] \cdot 4H_2O$ compound [19]. The concentration of Eu^{III} ion in the crystals was determined complexometrically (4.943 M). The crystal density was measured by the flotation method in a CH_3Cl/CH_3Br mixture ($d^{20} = 1.982$ g cm^{-3}). A solution of the Eu^{III}-acetate complex ($c_{Eu} = 0.2221$ M, $c_{acetate} = 4.078$ M, pH 4.70) was prepared by mixing $Eu(ClO_4)_3$ with an acetate buffer. A solution of 0.6531 M $Eu(ClO_4)_3$ (pH 2.30) was used as an aquoion standard. The refractive index (n) of the investigated crystals was 1.49, while that of the Eu^{III}-acetate solution was 1.33 and that of the aquoion 1.36.

Electronic absorption spectra were recorded on a Cary 5 spectrophotometer equipped with an Oxford CF 1204 continuous flow helium cryostat at 293 and 4 K.

Intensity calculations of the f–f transitions, pertinent to the Judd–Ofelt theory [20,21], were performed according to the procedures outlined [7–9]. The square of the unit

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tensor matrix elements were those given by Carnall et al. [16].

3. Results and discussion

The electronic absorption spectra of Eu^{III}-acetate in the single crystal and in solution as well as of the Eu^{III}-aquoion were measured in the range 240–650 nm. The splittings of the $^7F_0 \to {}^5D_2$, $^7F_0 \to {}^5D_1$ and $^7F_0 \to {}^5D_0$ transitions of the crystal at room and liquid helium temperatures clearly indicate one metal ion site of low symmetry, which is consistent with the X-ray findings [19]. Similarities between the absorption spectra of the Eu^{III}-acetate system in both phases are observed. In comparison to the absorption spectra of the Eu^{III}-acetate in the crystal and in solution, the maxima of the f–f bands of the aquoion are shifted towards the UV region. The energies and half-widths of the $^7F_0 \to {}^5D_0$ bands of the investigated systems amount to 17 274 and 16 cm^{-1} for the aquoion, 17 259 and 17 cm^{-1} for the acetate complex in solution, 17 252 and 5 cm^{-1} for the Eu^{III}-acetate crystal at 293 K and 17 240 and 3 cm^{-1} for the crystal at 4 K, respectively. Broadening of the $^7F_0 \to {}^5D_0$ bands in the case of the solution spectra arise from slightly varying metal ion environments.

The oscillator strength values (P_{exp}) of all f–f transitions of the investigated systems are given in Table 1. The two $^7F_1$ and $^7F_2$ excited states are partially populated at room temperature. Their populations were taken into account in calculations of the oscillator strength values of transitions from the $^7F_0$ ground state (P_{cor}). These values are also included in Table 1. Since some transitions are very weak, their intensities could be determined only with large errors. In such cases, the average values of the optical density from at least two measurements were taken for the calculation of the oscillator strength value.

It can be seen from Table 1 that the intensities of the f–f transitions which obey the selection rules of the hypersensitive transition ($\Delta J = 0, \pm 2$) are much higher for the Eu^{III}-acetate system in both phases than for the aquoion

Table 1
Oscillator strength values (P_{exp}, P_{cor}) for Eu^{III}-aquoion and Eu^{III}-acetate complexes in solution and in the crystal

Transition(s)	Aquoion		Eu^{III}-acetate solution		Eu^{III}-acetate crystal		
	$10^8 \cdot P_{exp}$	$10^8 \cdot P_{cor}$	$10^8 \cdot P_{exp}$	$10^8 \cdot P_{cor}$	293 K		4 K $10^8 \cdot P_{exp}$
					$10^8 \cdot P_{exp}$	$10^8 \cdot P_{cor}$	
$^7F_2 \to {}^5D_0$			0.47		0.13		
$^7F_1 \to {}^5D_0$	1.15		1.29		0.76		
$^7F_0 \to {}^5D_0$	≈0.004	≈0.006	0.17	0.27	0.10	0.15	0.03
$^7F_2 \to {}^5D_1$	0.10		0.22		0.16		
$^7F_1 \to {}^5D_1$	0.71		8.13		7.62		
$^7F_0 \to {}^5D_1$	1.53	2.41	1.52	2.42	1.47	2.26	0.28
$^7F_2 \to {}^5D_2$	0.09		0.45		0.37		
$^7F_1 \to {}^5D_2$	0.19		1.18		0.96		
$^7F_0 \to {}^5D_2$	2.30	3.62	24.74	39.43	15.56	23.95	4.00
Vibronic transition			0.36		0.56		0.55
$^7F_1 \to {}^5D_3$	2.61		6.89		5.67		
$^7F_0 \to {}^5D_3$	0.03	0.05	0.15	0.24	0.23	0.35	0.25
$^7F_0 \to {}^5L_6$	200.72	316.28	199.57	318.04	183.06	281.80	233.52
$^7F_{0,1} \to {}^5G_{6,5,4,3}, {}^5L_7, {}^5G_2$ [a]	110.34		128.33		115.17		74.54
$^7F_0 \to {}^5G_2$			7.78	12.26	9.26	14.26	3.13
$^7F_0 \to {}^5G_{6,5,4}$	38.07	59.99	40.45	64.46	35.18	54.16	55.87
$^7F_1 \to {}^5D_4$	3.29		3.88		3.83		
$^7F_0 \to {}^5D_4$	19.48	30.70	22.15	35.30	17.65	27.17	20.60
$^7F_{0,1} \to {}^5H_{6,5,4,7,3}$ [a]	126.35		109.08		109.39		109.73
$^7F_0 \to {}^5H_{6,5,4}$	88.88	140.05	86.91	138.50	78.69	121.14	90.67
$^7F_0 \to {}^5F_2$	3.25	5.12			25.03	38.53	26.89
$^7F_0 \to {}^5F_4$	57.59	90.75			32.56	50.12	48.62
$^7F_0 \to {}^5I_4$	18.96	29.88			11.99	18.46	9.86
$^7F_0 \to ({}^5I, {}^5H)_6$	51.14	80.58			44.88	69.06	54.70

[a] P_{exp} at 4 K determined in the same spectral range as at 293 K.

Table 2
Oscillator strength values of P_{cor} and P_{cal}, Ω_λ intensity parameters and rms deviation for Eu^{III}-aquoion and Eu^{III}-acetate complexes in solution and in the crystal

$^7F_0\rightarrow$	Aquoion				Solution		Crystal				
	$10^8 \cdot P_{cor}$	$10^8 \cdot P_{cal}$	$10^8 \cdot P_{cal}$	$10^8 \cdot P_{cal}$	$10^8 \cdot P_{cor}$	$10^8 \cdot P_{cal}$	$10^8 \cdot P_{cor}$	$10^8 \cdot P_{cal}$	$10^8 \cdot P_{cal}$	$10^8 \cdot P_{cal}$	$10^8 \cdot P_{cal}$
$(^5I,^5H)_6$ $[U^{(6)}]$[a]	80.58	45.79					69.06	41.17			
$^5I_4$ $[U^{(4)}]$	29.88	14.66					18.46	8.21			
$^5F_4$ $[U^{(4)}]$	90.75	81.89	80.32				50.12	45.86	44.89	44.89	
$^5F_2$ $[U^{(2)}]$	5.12	3.66	3.66				38.53	25.89	25.89	21.17	
$^3H_{6,5,4}$ $[U^{(4)},U^{(6)}]$	140.05	164.75	162.44	147.00	138.50	149.37	121.14	138.48	136.70	136.70	128.99
$^5D_4$ $[U^{(4)}]$	30.70	21.83	21.41	7.06	35.30	8.35	27.17	12.24	11.99	11.99	4.81
$^5G_{6,5,4}$ $[U^{(4)},U^{(6)}]$	59.99	91.15	89.89	83.31	64.46	84.55	54.16	77.69	76.71	76.71	73.42
$^5G_2$ $[U^{(2)}]$							14.26			25.01	
$^5L_6$ $[U^{(6)}]$	316.28	302.48	298.57	307.17	318.04	307.99	281.80	272.18	269.01	269.01	273.32
$^5D_2$ $[U^{(2)}]$	3.62	4.75	4.75	3.62	39.43	39.43	23.95	33.67	33.67	27.54	23.95
$\Omega_2 \cdot 10^{20}/cm^2$		2.10 ± 8.31	2.10 ± 7.65	1.60 ± 10.99		17.60 ± 11.59		13.58 ± 6.29	13.58 ± 6.04	11.11 ± 4.64	9.66 ± 9.04
$\Omega_4 \cdot 10^{20}/cm^2$		5.47 ± 1.43	5.36 ± 1.33	1.77 ± 3.76		2.11 ± 3.97		2.79 ± 1.08	2.74 ± 1.05	2.74 ± 1.00	1.10 ± 3.10
$\Omega_6 \cdot 10^{20}/cm^2$		5.85 ± 0.41	5.78 ± 0.38	5.94 ± 0.47		6.03 ± 0.49		4.81 ± 0.31	4.75 ± 0.30	4.75 ± 0.28	4.83 ± 0.38
$rms \cdot 10^8$		23.71	21.84	24.84		25.97		19.68	18.88	17.90	22.41

[a] $U^{(\lambda)}$ matrix elements used for calculations of Ω_λ parameters.

($^7F_0 \rightarrow {}^5F_2, {}^5D_2, {}^5D_0$; $^7F_1 \rightarrow {}^5D_3, {}^5D_1$; $^7F_2 \rightarrow {}^5D_2, {}^5D_0$). This indicates that the Eu^{III}-acetate complex both in the crystal and in solution has a distinctly lower symmetry than the aquoion. For the Eu^{III}-acetate crystal, as for other lanthanide acetates, the intensities of these transitions are much greater than those for the crystals of Eu^{III}-trichloroacetate [13,14] and trifluoroacetate [14]. A rather good correspondence between the oscillator strength values of the Eu^{III}-acetate system in the crystal and in solution may be seen from examination of the values given in Table 1. The only exception to this correspondence is the larger oscillator strength value of the $^7F_0 \rightarrow {}^5D_2$ hypersensitive transition for the Eu^{III}-acetate complex in solution in comparison to that in the crystal.

The absorption spectra of the crystal at 293 and 4 K were recorded with the same crystal position with respect to the incident light beam. It can be seen from Table 1 that the intensities of the $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_0$ transitions strongly decrease on reducing the temperature to 4 K, while the decrease in intensities of the f–f transitions in the 280–415 nm spectral region is about 25% at 4 K according to P_{cor} at 293 K. Since no changes were observed in the spectra while heating the crystal from 4 to 293 K one may assume the absence of phase transitions. Most probably, this unusual behaviour of the three above-mentioned f–f intensities is caused by crystal anisotropy. The spectra of these transitions were also measured in polarized light. While the energies of all crystal field components do not change, the ratio of the intensity distribution among the particular components depends distinctly on the polarization of the incident light. This, in turn, results in an intensity change at 293 K of about ±20, ±4 and above ±50% for the $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$ and the weakest $^7F_0 \rightarrow {}^5D_0$ transition, respectively.

The Ω_λ intensity parameters of the analyzed systems presented in Table 2 were determined for different sets of transitions. It can be seen from Table 2 that the elimination of some spectral intensities of the f–f transitions in the UV region with non-zero $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$ matrix elements does not influence the Ω_6 value and affects the Ω_4 parameter value much more than the Ω_2 value. Such a comparison was possible owing to the registration of the absorption spectra of the investigated systems in the UV range (Fig. 1). A larger value of the Ω_2 parameter for Eu^{III}-acetate in solution as compared to the Ω_2 value of the crystal confirms a greater perturbation of the Eu^{III} inner sphere in solution, caused by equilibria between different species. The proximity of the Ω_4 and Ω_6 parameters in the limit of the calculated error for both acetate systems may indicate that species which exist in solution do not differ

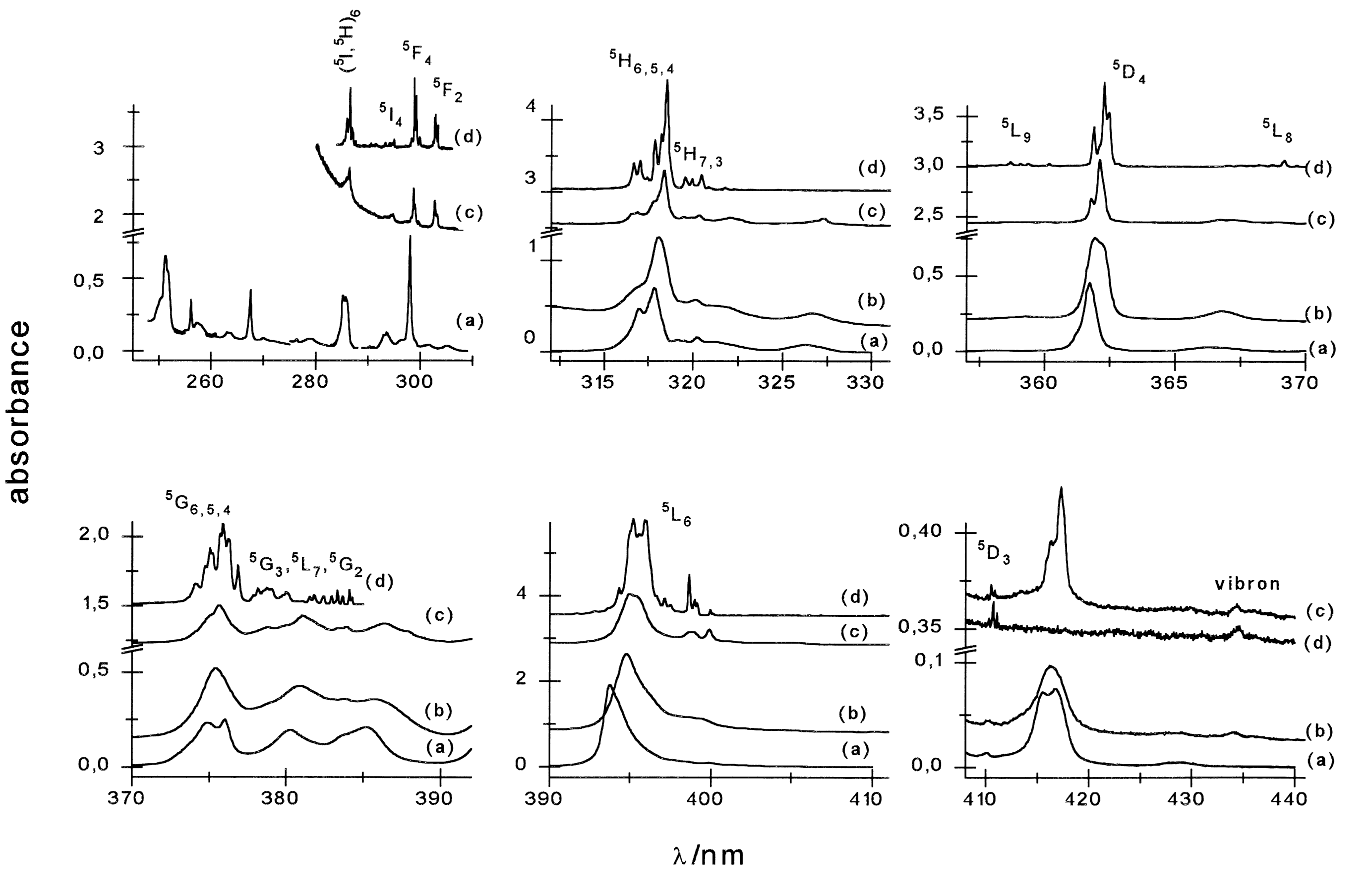

Fig. 1. Absorption spectra of Eu^{III}-aquoion (a), Eu^{III}-acetate complex in solution (b) and in the crystal at 293 K (c) and at 4 K (d): (a) $c_{Eu}^{III} = 0.6531$ M, pH 2.30, $d = 1$ cm (240–410 nm), $d = 4$ cm (408–442 nm); (b) $c_{Eu}^{III} = 0.2221$ M, $c_{acetate} = 4.078$ M, pH 4.70, $d = 4$ cm; (c,d) $c_{Eu}^{III} = 4.943$ M, $d = 0.107$ cm.

significantly in polarizability of the ligand and metal–ligand distances from that found in the crystal. This is consistent with the analysis of spectral intensities of the f–f transitions as well as the energies and half-widths of the $^7F_0 \rightarrow {}^5D_0$ bands for the Eu^{III}-acetate complex in both phases. Extension of Eu^{III}-acetate crystal studies is underway.

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