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Spectroscopy of $LnBr_3 \cdot 6H_2O$ at room and helium temperature

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Abstract

The lanthanide (Nd, Eu) tribromide hexahydrate monocrystals have been obtained from water solutions. Absorption, excitation and emission spectra at room and low temperatures are reported. The probabilities of f–f transitions have been analysed on the basis of the Judd–Ofelt theory. The temperature dependence of intensity was found and the contribution of vibronic coupling in f–f transitions was considered. The Stark components in optical lines were determined and vibronic bands were assigned. The intensities of vibronic transitions are briefly discussed in terms of existing theories. The results obtained are compared with spectroscopic data for other neodymium monomeric compounds.

1. Introduction

Recently a great effort has been made to elucidate the vibronic components in the luminescence and absorption spectra of lanthanide compounds. The vibronic coupling is usually observed in centrosymmetric single crystals. Recently, however, it was stated that vibronic components appeared in spectra of non-centrosymmetric lanthanide sites [1–4]. A temperature dependence of the intensity was found in the spectra of the series of lanthanide carboxylates and the vibronic coupling was considered [5, 6]. All these compounds form polymeric or dimeric structures. The single crystals of bromides of the 4f and 5f metals are assumed to be isomorphic with $LnCl_3 \cdot 6H_2O$ [7, 8]. Thus, in $NdBr_3 \cdot 6H_2O$ two Br^- ions are inner-sphere ions and C_{2v} point symmetry of the Ln^{3+} ion could be stated on the basis of X-ray data for $GdCl_3 \cdot 6H_2O$ [9] and $NdCl_3 \cdot 6H_2O$ [10]. Zolin and coworkers [11], in a luminescence investigation of $EuCl_3 \cdot 6H_2O$ crystals, confirmed C_{2v} symmetry for the Eu^{3+} ion. Since for the gaseous $LnBr_3$ and LnI_3 the extremely high intensity of the hypersensitive transition was explained by the vibronic mechanism [12], it seemed reasonable to investigate the spectroscopy of single crystals of lanthanide bromides to elucidate vibronic coupling in the electronic band intensity.

2. Experimental details

The monocrystals of lanthanide tribromide hexahydrates $LnBr_3 \cdot 6H_2O$ were grown from aqueous solutions.

The concentration of Nd^{3+} and Eu^{3+} ions was determined complexometrically using xylenol orange as the end-point indicator [13]. The crystals of neodymium compounds were checked using Weissenberg measurement (monoclinic, $a = 8.204$ Å, $b = 6.757$ Å, $c = 10.002$ Å, $\beta = 93.39°$).

The crystal density $\rho = 2.86$ g cm^{-3} for $NdBr_3 \cdot 6H_2O$ was measured by the flotation method using tribromomethane and *sym*-tetrabromoethane.

Absorption spectra were recorded on Beckman UV 5240 and Cary 5 spectrophotometers in the 1750–310 nm range at 293, 223, 173, 143, 113 and 5 K. The room temperature spectra were recorded for different single-crystal orientations. An Aminco SPF-500 spectrofluorometer was used for luminescence and excitation spectra detection at 77 K. Judd–Ofelt theory was applied to the intensity analysis and τ_λ parameters were calculated according to the procedure described in refs. 14 and 15.

3. Results and discussion

Absorption spectra of $NdBr_3 \cdot 6H_2O$ single crystals for two different orientations at room temperature are shown in Fig. 1. Detailed identification of the observed transitions and the corresponding values of the oscillator strength are listed in Table 1.

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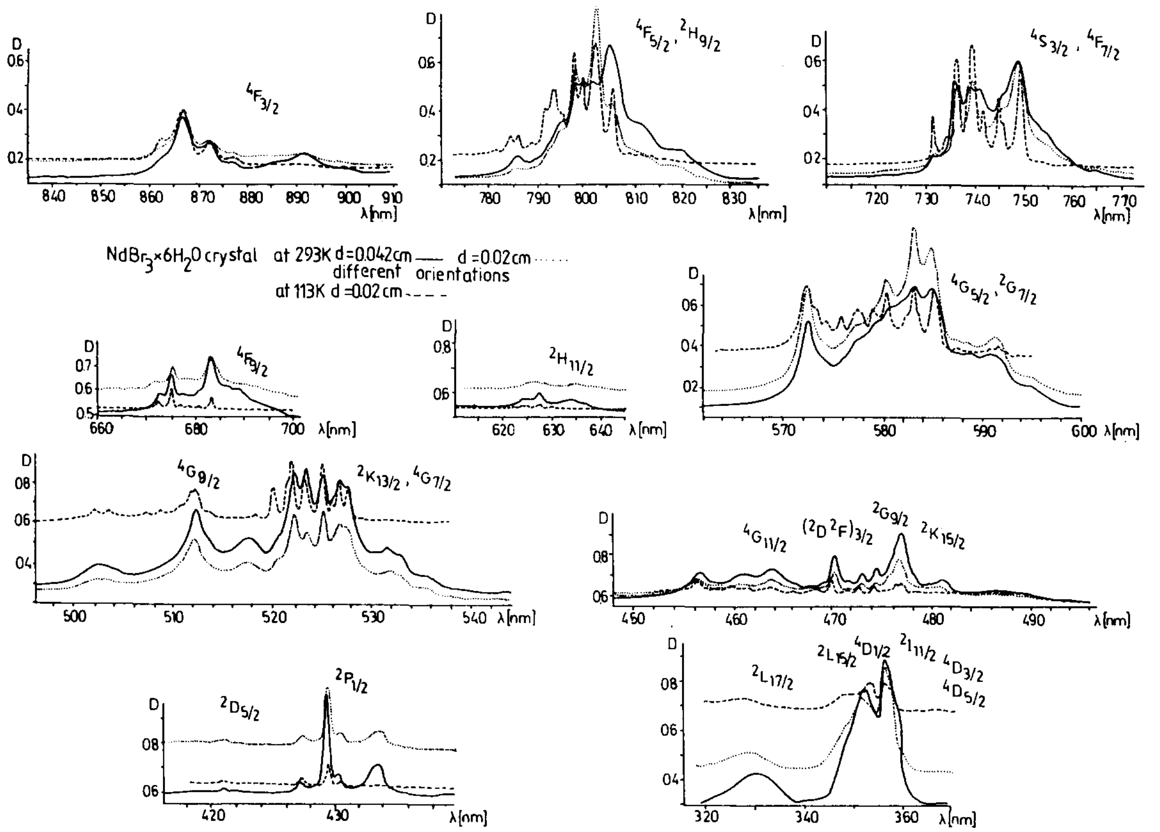

Fig. 1. Absorption spectra of $NdBr_3 \cdot 6H_2O$ crystal at 293 K in different orientations and at 113 K with identification of 4f–4f transitions.

TABLE 1. The oscillator strength values P and the τ_λ parameter values calculated from Judd's relation for $NdBr_3 \cdot 6H_2O$ crystal at room (different orientations a, b, c) and low temperatures

S', L', J'	$P \times 10^8$ at the following temperatures							
	293 K (orientation a)	293 K (orientation b)	293 K (orientation c)	223 K	173 K	143 K	113 K	5 K
$^4F_{3/2}$	144.94	164.24	225.67		244.84		163.51	110.61
$^4F_{5/2}$, $^2H_{9/2}$	477.87	592.74	786.13		600.54		514.69	147.49
$^4F_{7/2}$, $^4S_{3/2}$	493.44	627.01	801.31		639.78		530.02	184.15
$^4F_{9/2}$	47.72	50.85	53.98		44.63		45.76	21.28
$^2H_{11/2}$	11.72	15.65	19.57		20.55		21.39	6.96
$^4G_{5/2}$, $^2G_{7/2}$	1352.80	1606.08	2007.73	1370.83	1339.73	1283.46	1073.59	372.09
$^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$	559.63	604.96	741.80		654.77		576.43	146.74
$^2K_{15/2}$, $^2G_{9/2}$, $(^2D, {}^2F)_{3/2}$, $^4G_{11/2}$	144.56	157.15	172.37		162.12		180.48	60.35
$^2P_{1/2}$, $^2D_{5/2}$	31.95	31.51	38.96		34.40		35.36	11.08
$^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$, $^2L_{15/2}$	718.66	856.93	983.99		756.16		562.48	284.78
$^2I_{13/2}$, $^4D_{7/2}$, $^2L_{17/2}$	154.74	165.96	169.70		181.27		116.70	
$\tau_2 \times 10^9$	5.21 ± 0.53	6.18 ± 0.53	8.04 ± 0.55		$\tau_2^* \times 10^9$		6.54 ± 0.57	
$\tau_4 \times 10^9$	4.20 ± 0.48	4.90 ± 0.48	5.55 ± 0.49		$\tau_4^* \times 10^9$		4.58 ± 0.52	
$\tau_6 \times 10^9$	5.65 ± 0.69	7.30 ± 0.69	9.24 ± 0.71		$\tau_6^* \times 10^9$		8.97 ± 0.90	

τ_λ^* values are mean τ_λ values.

The change in the single-crystal orientation leads to significant changes in individual components of the f–f transition intensity. The shape of the bands differs especially in the regions of $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$; $^4F_{7/2}$, $^4S_{3/2}$ transitions and of hypersensitive transitions, which is valid for each spectrum. Since the $NdBr_3 \cdot 6H_2O$ and $EuBr_3 \cdot 6H_2O$ single crystals are biaxial, such an effect can be observed.

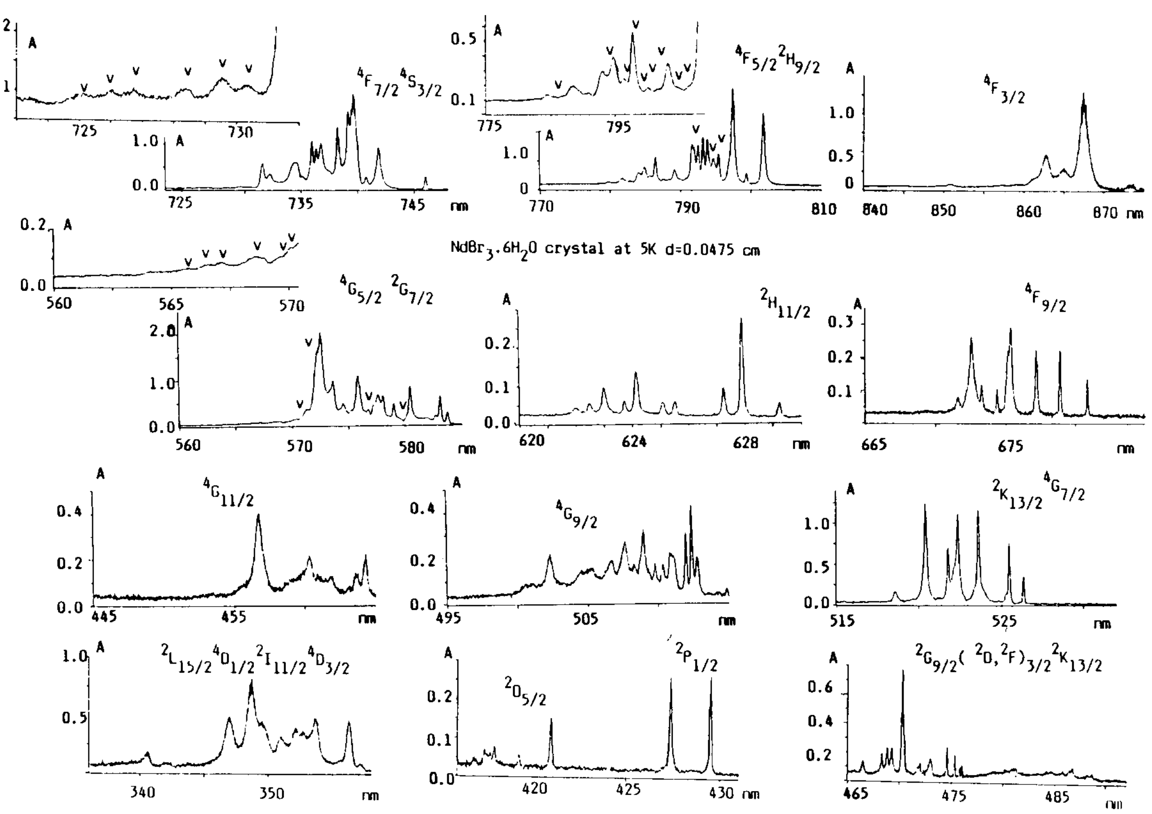

Fig. 2. Absorption spectra of $NdBr_3 \cdot 6H_2O$ crystal at 5 K with identification of 4f–4f transitions.

The values of the oscillator strengths and calculated τ_λ parameters are summarized in Table 1. Judd's equation [16] contains neither polarization nor angular terms so the total integrated absorbances are required in order to fit the theory. Since significant fluctuations of intensity for the different single-crystal orientations were found, in intensity analysis the mean values of the oscillator strengths were used (from three orientations of single crystals). The values of the oscillator strengths P_{cal} were evaluated theoretically by a fitting procedure within the framework of the Judd–Ofelt theory [16, 17]. It is noteworthy that greater intensity changes of the two transitions: $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4S_{3/2}$; $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$ result in the decrease in the τ_6 parameter. Such effects have never been observed by us in our studies before.

The low temperature (113, 5 K) spectra are presented in Fig. 1 and Fig. 2. They reveal a rich fine structure especially for the hypersensitive transition and $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$; $^4F_{7/2}$, $^4S_{3/2}$.

The oscillator strength values of f–f transitions at room temperature are comparable with those for aquo ion, but the intensity of the hypersensitive transition differs significantly. This intensity is higher than that of distorted octahedral neodymium hexahalide $[(C_6H_5)_3PH]_3NdCl_6$ [18]. Unfortunately, the intensities of non-centrosymmetric neodymium single crystals are known for only a few cases. In other cases (Nd^{3+}-doped crystals) the metal ions usually occupy more than one site; their intensity is known but the intensities for a particular site symmetry have been determined for few systems only [21]. The neodymium nitrates and chloroacetates and some neodymium carboxylates (amino acid system), with a well-determined point symmetry of the Nd^{3+} ion, were recently investigated by others and by us [5, 6, 19, 20]. All carboxylates form polymeric or dimeric structures with variable Ln–O distances and distortion from the ideal polyhedron. Consequently two or more site symmetry positions may be considered for those systems [5]. The symmetry of those positions in the same single crystal does not vary too much. Thus the intensity for separate sites does not change significantly.

Intensities of monomeric centrosymmetric and non-centrosymmetric single crystals of simple lanthanide salts are known for only a few systems [1, 2, 18, 22]. Since in our case the C_{2v} point symmetry can be expected, the observed intensity could be related to that of neodymium carboxylate with C_{2v} symmetry [5].

A decrease in intensity for the chosen transitions with temperature decrease was observed. This could be due to both a change in the population of the Stark components of the ground state and a contribution of the vibronic mechanism in transitions. If the first reason is responsible, we will observe almost the same change

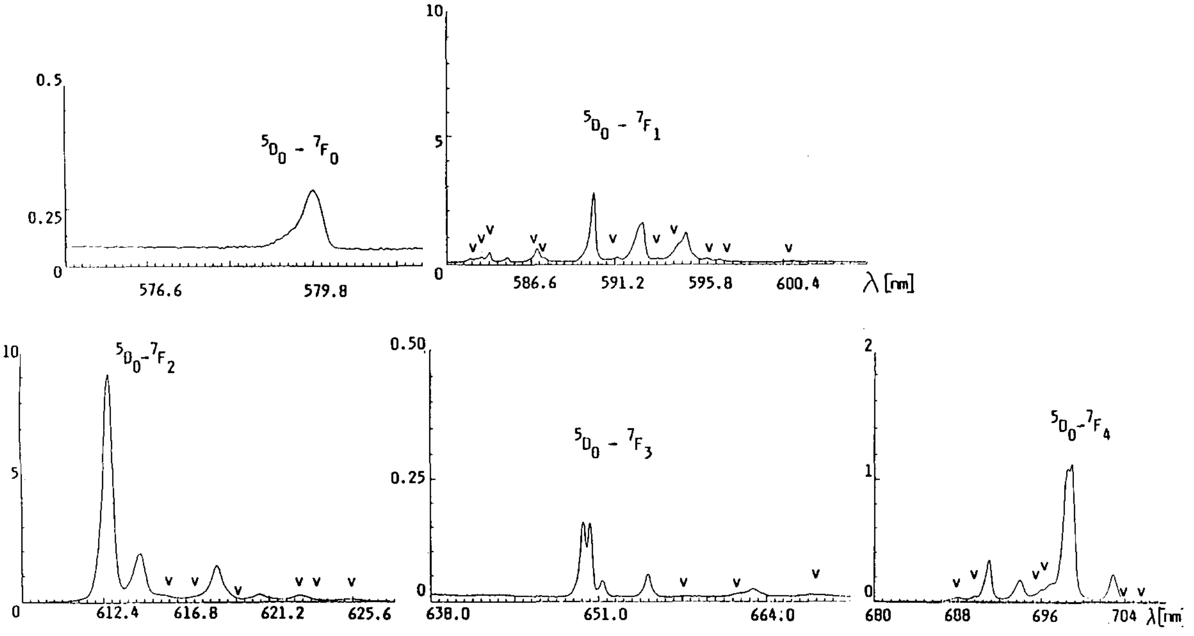

Fig. 3. Luminescence spectra of $EuBr_3 \cdot 6H_2O$ crystal at 77 K.

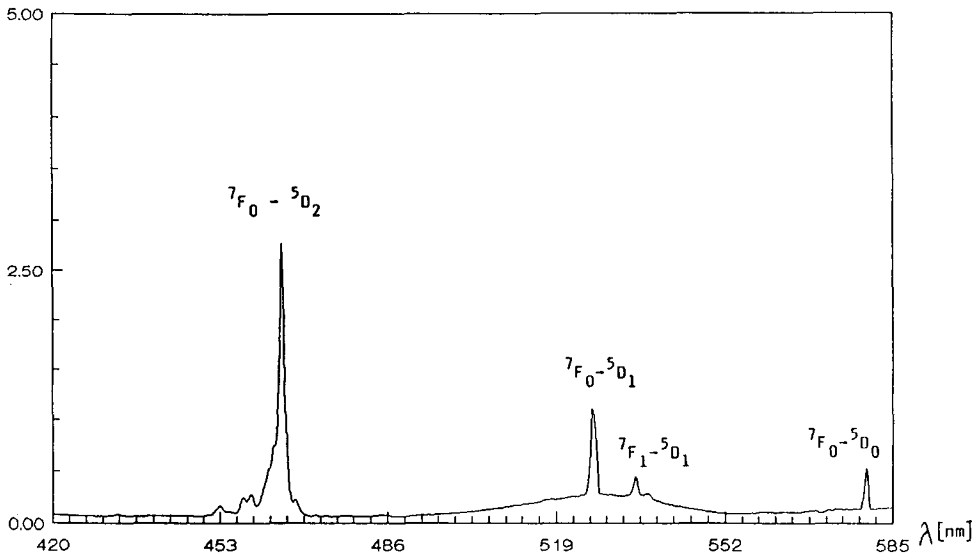

Fig. 4. Excitation spectrum of $EuBr_3 \cdot 6H_2O$ crystal at 77 K.

in oscillator strength for all the transitions detected. In fact for only a few transitions were significant variations in oscillator strength values found (Table 1). It is noteworthy that the variation in intensity is higher for $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions than for $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$; $^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$, $^2L_{15/2}$. According to the vibronic transition theory for lanthanide ions the increase in intensity can only be found for transitions [23–25] which obey the selection rule $\Delta J = 0, 2$. However, Kirby and Richardson have found fine vibronic structures in almost all transitions of Eu^{3+} ions, in the spectra of non-centrosymmetric compounds [1, 2].

Vibronic structure has been observed in crystal spectra of a large number of lanthanide compounds [25–32]. The proportion of vibronic to electron intensity varies with the ligands or crystal host, and also with the particular lanthanide ions considered [33, 34]. Temperature variation of the intensities of lanthanide spectra has been studied by Gruber *et al.* for neodymium hexachlorocomplexes [18], and by us for some amino acid single crystals [5]. Gruber *et al.* have found that the intensities of the individual Stark components of all the accessible absorption bands are temperature invariant. However, the spectrum of Tm^{3+} ethylsulphate has been measured at 300 and 23 K [26] and it has been shown that the oscillator strengths of electronic transitions are temperature dependent, revealing thus the considerable vibronic contribution. Since in our

TABLE 2. Stark components of electronic lines and energies of vibration modes composed with them in $NdBr_3\cdot 6H_2O$ crystal at 5 K

	Wavenumber (cm^{-1})	
$^4I_{9/2}\rightarrow{}^4F_{5/2}$, $^2H_{9/2}$	12473+100	ν_{Nd-Br}
	+112	
	+135	
	+146	
	+199	δ_{O-Nd-O}
	+212	
	+300	ν_{Nd-O}
	+319	
	+333	
	+352	
	12511+112	ν_{Nd-Br}
	+205	δ_{O-Nd-O}
	+307	ν_{Nd-O}
	12540+105	ν_{Nd-Br}
	+118	
	+188	δ_{O-Nd-O}
	+201	
	+215	
$^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$	17131+141	ν_{Nd-Br}
	+193	δ_{O-Nd-O}
	+208	
	+218	
	+339	ν_{Nd-O}
	+552	ω_{Nd-OH_2}
	17150+356	ν_{Nd-O}
	17228+305	ν_{Nd-O}
	+313	
	+326	
	+359	
	17313+319	ν_{Nd-O}
	+335	

TABLE 3. Stark components of electronic lines and energies of vibration modes composed with them in $EuBr_3\cdot 6H_2O$ crystal at 77 K

	Wavenumber (cm^{-1})	
$^5D_0\rightarrow{}^7F_0$	17247−103	ν_{Eu-Br}
	−118	
	−134	
	−210	δ_{O-Eu-O}
	−221	
	−320	ν_{Eu-O}
$^5D_0\rightarrow{}^7F_1$	16948−100	ν_{Eu-Br}
	−131	
	−195	δ_{O-Eu-O}
	−306	ν_{Eu-O}
	16872−101	ν_{Eu-Br}
$^5D_0\rightarrow{}^7F_2$	16321−123	ν_{Eu-Br}
	−333	ν_{Eu-O}
	−1121	δ_{Eu-OH_2}
	16276−129	ν_{Eu-Br}
	−336	ν_{Eu-O}
	−1168	δ_{Eu-OH_2}
	16168−111	ν_{Eu-Br}
	−119	
	−1184	δ_{Eu-OH_2}
$^5D_0\rightarrow{}^7F_3$	15271−737	ρ_{Eu-OH_2}
	−771	
$^5D_0\rightarrow{}^7F_4$	14473−106	ν_{Eu-Br}
	−127	
	14316−119	ν_{Eu-Br}
	−132	

studies of the investigated single crystals the biggest changes in intensity (about 72.5% from orientation a) were observed for hypersensitive transition (see Table 1), this is probably caused by the vibronic mechanism.

In the single crystals under investigation the lanthanide ions occupy one site symmetry position (crystals belong to the same class of structure as $LnCl_3\cdot 6H_2O$), and thus the additional lines observed in the spectrum at 5 K can be due to the vibration components (see Fig. 2). Figures 3 and 4 show emission and excitation spectra of $EuBr_3\cdot 6H_2O$ crystals at 77 K. Vibronic coupling is well demonstrated in $^7F_0\rightarrow{}^5D_0$; $^5D_2$ and $^5D_0\rightarrow{}^7F_0$; $^7F_2$ transitions in excitation and emission spectra respectively. Assignments of particular vibronic components were made using the IR data [35]. Results are presented in Tables 2 and 3.

Only those vibronic components which were observed in absorption, emission and excitation spectra in both neodymium and europium compounds are compiled. It should be noted that intensities of vibronic components are higher in excitation spectra than in the emission spectra, calculated from the $^5D_2$:$^5D_1$ and $^7F_2$:$^7F_1$ transition ratios (4.60 and 2.35). A similar effect was observed by Van Vliet and Blasse in crystals of $Na_5[(Gd,Eu)(WO_4)_4]$ and explained assuming a tentative model involving mixing of the ^7F and ^7CTS levels of the Eu^{3+} ion [36]. In our case it can be caused by ^7F and ^7CTS levels of Eu^{3+} (from the Br^- ion) and by the other factor of the relation describing the oscillator strength of vibronic transitions considered by Van Vliet and Blasse [36].

As well as the vibronic components included in Table 2, one can find additional lines which appear in almost all electronic bands. The origin of those additional components could be the cooperative effect of Ln–Ln ion interaction to $R=9$ Å [37–39]. The crystal structure data tended to confirm this type of interaction. However, further spectroscopic investigation of diluted single crystals is needed [35].

On the contrary, the vibronic components in their nature are usually drastically less intense than electronic transitions. In fact, in the optical spectrum of the studied compounds at 5 K in the region of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition we can find as well as two low intense components two other strong components with the same intensity, separated by 113 cm^{-1}. The appearance of those two strong components could be explained by lanthanide ions occupying two site symmetry positions. This was not exhibited in X-ray data.

It is worth mentioning that in our earlier studies of single crystals with amino acids, where lanthanide ions occupy two or four different site symmetry positions, two or four components of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition were separated by about 11 cm^{-1} and about 22 cm^{-1}. This is obviously less drastic than our present observation. Those two components are seen also at almost the same energies in the spectra at 300 and 113 K but with different intensities. Furthermore, the energy of separation (about 113 cm^{-1}) of the two components corresponds to the Nd–Br vibration mode in IR spectra. Such a phenomenon can lead to the population of the second component of the $^4I_{9/2}$ state and as a consequence one observes a transition from two Stark components of the ground state.

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References

1 A.F. Kirby and F.S. Richardson, *J. Phys. Chem., 87* (1983) 2544.
2 A.F. Kirby and F.S. Richardson, *J. Phys. Chem., 87* (1983) 2557.
3 E. Antic-Fidancev, M. Lemaitre-Blaise and P. Caro, *C.R. Acad. Sci. Paris, 298* (1984) 575.
4 E. Antic-Fidancev, M. Lemaitre-Blaise, P. Caro, B. Piriou and W. Stręk, in B. Jeżowska-Trzebiatowska, J. Legendziewicz and W. Stręk (eds.), *Rare Earth Spectroscopy,* World Scientific, Singapore, 1985, p. 354.
5 J. Legendziewicz, T. Głowiak, E. Huskowska and Dao Cong Ngoan, in B. Jeżowska-Trzebiatowska, J. Legendziewicz and W. Stręk (eds.), *Rare Earth Spectroscopy,* World Scientific, Singapore, 1985, p. 146.
6 J. Legendziewicz, T. Głowiak, E. Huskowska and Dao Cong Ngoan, *Polyhedron, 7* (1988) 2495.
7 D. Brown, S. Fletcher and D.G. Holah, *J. Chem. Soc. A,* (1968) 1889.
8 J.C. Barnes and G.Y.R. Nicoll, *Inorg. Chim. Acta, 110* (1985) 47.
9 M. Marezio, H.A. Plettinger and W.H. Zachariasen, *Acta Crystallogr., 14* (1961) 234.
10 A. Habenschuss and F.H. Spedding, *Cryst. Struct. Commun., 9* (1980) 71.
11 M.I. Gajduk, W.F. Zolin and L.S. Gaigerova, *Luminescence Spectra of Europium,* Nauka, Moscow, 1974.
12 D.M. Gruen, C.W. DeKock and R.L. McBeth, *Adv. Chem. Ser., 71* (1967) 102.
13 S.J. Lyle and M. Rahman, *Talanta, 10* (1963) 1177.
14 J. Legendziewicz, G. Oczko and B. Keller, *Bull. Pol. Acad. Sci., 34* (1986) 257.
15 J. Legendziewicz, G. Oczko, B. Keller and B. Jeżowska-Trzebiatowska, *Mater. Sci., 14* (1988) 15.
16 B.R. Judd, *Phys. Rev., 127* (1962) 750.
17 G.S. Ofelt, *J. Chem. Phys., 37* (1962) 511.
18 J.B. Gruber, E.R. Menzel and J.L. Ryan, *J. Chem. Phys., 51* (1969) 3816.
19 J. Legendziewicz, G. Meyer and G. Oczko, *Polyhedron, 10* (1991) 1921.
20 W.T. Carnall, S. Siegel, J.R. Ferraro, B. Tani and E. Gebert, *Inorg. Chem., 12* (1973) 560.
21 O.L. Malta, A.A.S. Da Gama and S. Canuto, *Rev. Bras. Fis., 12* (1982) 563.
22 J.J. Dallara, M.F. Reid and F.S. Richardson, *J. Phys. Chem., 88* (1984) 3587.
23 B.R. Judd, *Phys. Sci., 21* (1980) 543.
24 W. Stręk, in B. Jeżowska-Trzebiatowska, J. Legendziewicz and W. Stręk (eds.), *Rare Earth Spectroscopy,* World Scientific, Singapore, 1985, p. 636.
25 T.R. Faulker and F.R. Richardson, *Mol. Phys., 35* (1978) 1841.
26 J. Dexport-Ghys and F. Auzel, *J. Chem. Phys., 80* (1984) 4003.
27 I. Richman, R.A. Satten and E.Y. Wong, *J. Chem. Phys., 39* (1963) 1833.
28 W.F. Krupke and J.B. Gruber, *Phys. Rev., 139* (1965) A2008.
29 N. Yamada and S. Shivnoya, *J. Phys. Soc. Jpn., 31* (1971) 841.
30 Hao Zhiran, G.J. Dirksenand and G. Blasse, *J. Solid State Chem., 52* (1984) 130.
31 G. Blasse, G.J. Dirksen and J.P.M. Van Vliet, *Recl. Trav. Chim. Pays-Bas, 107* (1988) 138.
32 G. Blasse, G.J. Dirksen and J.P.M. Van Vliet, *Inorg. Chim. Acta, 142* (1988) 165.
33 G. Blasse and L.H. Brixner, *Inorg. Chim. Acta, 169* (1990) 25.
34 R.D. Peacock, *Struct. Bonding, 22* (1975) 83.
35 J. Legendziewicz, G. Oczko and J. Hanuza, in preparation.
36 J.P.M. Van Vliet and G. Blasse, *J. Solid State Chem., 85* (1990) 56.
37 G. Blasse, *Inorg. Chim. Acta, 169* (1990) 33.
38 M. Dahl and G. Schaack, *Phys. Rev. Lett., 56* (1986) 3.
39 J. Legendziewicz and E. Huskowska, *Excited States of Transition Elements,* World Scientific, Singapore, 1989, p. 228.