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# Optical properties of single crystals of heavy lanthanide chlorides

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# ABSTRACT

Studies of heavy lanthanide chlorides may provide important information on the degree of  $Ln^{3+}$ –ligand bond covalency. Monocrystals of  $LnCl_3$ · $GH_2O$ , where Ln = Dy, Ho and Er, were grown and spectroscopic investigations were performed at room temperature and at low temperatures down to 4.2 K in order to understand the nature of the  $Ln^{3+}$ –L bonds. The intensities of the electronic lines and the Judd–Ofelt parameters were calculated and compared with those obtained for chlorides of light lanthanides (i.e. Ce(III), Pr(III) and Nd(III)). Room temperature Raman and IR studies of the compounds under investigation were also performed. The relationship between hypersensitivity and covalency is discussed. The change of vibronic coupling strength along the lanthanide ion series does not modify monotonically. The ion-pair interactions are especially visible for the  ${}^{5}I_8 \rightarrow {}^{5}F_2$  and  ${}^{5}I_8 \rightarrow {}^{5}F_3$  transitions in the HoCl<sub>3</sub>-GH<sub>2</sub>O low temperature spectra.

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### 1. Introduction

Studies on the nature of rare earth-ligand bonds is of great fundamental interest, especially with respect to the use of spectroscopy to probe the solution complexation properties of coordination complexes and biological systems [1]. Lanthanide halides as well as elpasolite-type crystals play a significant role both in fundamental investigations and in several areas of practical applications, such as linear and non-linear optics [2,3]. The spectroscopic studies of lanthanide coordination compounds in the crystalline phase, for which the inner sphere of the Ln<sup>3+</sup> ion is directly defined, are a very appropriate starting point for interpreting and understanding the spectral data of these compounds in solution. Spectral parameters determined on the basis of such studies may provide valuable information on the nature of lanthanide element-ligand (Ln<sup>3+</sup>-L) bonds. Although lanthanides form strong ionic bonds in complexes, a small degree of covalency has also been proposed [4]. It is not clear, however, which metal orbitals are involved in such covalent bonding.

It is obvious that the 4f electrons are not much affected by ligands, while the higher lying orbitals interact with adjacent atoms or ions. Nevertheless, some direct contribution of the 4f orbitals to the observed covalency is not always negligible [5]. In the lanthanide series from  $La^{3+}$  to  $Lu^{3+}$ , the ionic contribution to the metalligand bond increases at a slower rate than the covalent contribution, and it depends on the metal atomic number. This dependence is not linear [5]. One of the parameters that can determine the degree of  $Ln^{3+}-L$  bond covalency is the strength of the vibronic coupling for the 4f–4f transitions of the  $Ln^{3+}$  ions. Therefore, the quantitative estimation of the vibronic coupling is of great importance.

The aim of the present paper is to estimate the degree of  $Ln^{3+}-L$ bond covalency. Heavy lanthanide chloride monocrystals  $LnCl_3 \cdot 6H_2O$ , where Ln = Dy, Ho and Er, were synthesised. Spectroscopic investigations were adopted as the method to obtain insight into the nature of the  $Ln^{3+}-L$  bond. Additionally, the paper presents a correlation between the optical properties of the heavy lanthanide chlorides (for ions close to the end of the lanthanide series) in the solid state and the light lanthanide chlorides (for ions at the beginning lanthanide series) that we have investigated previously [6].

In the crystals of light lanthanide chlorides  $LnCl_3 \cdot 7H_2O$  (Ln = La, Pr), dimeric units with chloride bridges are formed [7,8]. However, heavier lanthanide chlorides of the type  $LnCl_3 \cdot 6H_2O$  (Ln = Nd to Lu) crystallise in the *P2/n* space group and form  $[LnCl_2(H_2O)_6]^+$  isolated polyhedra. Thus, a comparison of the spectroscopic behaviour of the investigated compounds in the solid state makes it possible to study ion-pair interactions and electron–phonon coupling, i.e. phenomena that were the subject of our recent papers [9–12].

## 2. Experimental

 $Ln_2O_3$  (Fluka, 99.99%) was dissolved in hydrochloric acid until a solution of pH 7 was achieved. The rare earth oxides and hydrochloric acid were of commercial grade and were used without further purification. Single crystals of  $LnCl_3$ · $GH_2O$  (where Ln = Dy, Ho and Er) of good optical quality were obtained by evaporation of the





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solutions. The contents of the lanthanide ions were determined by complexometric EDTA titration with xylenol orange as an indicator. All crystals were checked by X-ray diffraction and were found to be isostructural with other crystals of known structure [7,8].

The high resolution absorption spectra of single crystals of  $LnCl_3 \cdot GH_2O$ , where Ln = Dy, Ho and Er, were recorded within the spectral range 300–2200 nm at 293 K and 4.2 K using a Cary-Varian 500 UV–vis-near-IR spectrophotometer equipped with an Oxford CF 1204 continuous flow helium cryostat. Routinely, the single crystal spectra of the spectroscopically active ions were recorded in the 800–2200 nm range versus the respective thickness of the LaCl<sub>3</sub> \cdot GH<sub>2</sub>O crystals. The areas of the absorption bands were determined numerically by a graphical integration method and expressed in terms of the oscillator strengths using the method described in [13]:

$$P = 4.33 \times 10^{-9} \int_{\sigma_1}^{\sigma_2} \varepsilon(\sigma) d\sigma, \tag{1}$$

where  $\varepsilon(\sigma)$  is the molar extinction coefficient of the band at the wavenumber  $\sigma$  (cm<sup>-1</sup>). The experimental oscillator strength values were used for the calculation of the Judd–Ofelt parameters  $\tau_{\lambda}$  (cm) [14,15] according to the equation given by Carnall et al. [16,17]:

$$P = \sum_{\lambda=2,4,6} \tau_{\lambda} \sigma \left( f^{N} \Psi_{J} \| \mathbf{U}^{(\lambda)} \| f^{N} \Psi_{J'}' \right)^{2} / (2J+1),$$
(2)

where  $(f^N \Psi_J || \mathbf{U}^{(\lambda)} || f^N \Psi'_{J'})$  are the reduced matrix elements of the unit tensor operator  $\mathbf{U}^{(\lambda)}$  calculated by Carnall et al. [16,17] in the intermediate coupling scheme;  $f^N \Psi_J, f^N \Psi'_{J'}$  are the initial and final states of the electronic transition; and J is the total quantum number.

The room temperature infrared absorption spectra of  $LnCl_3$ · 6H<sub>2</sub>O, where Ln = Dy, Ho and Er, were measured using an FTIR Biorad 575C spectrometer in the spectral range 30–4000 cm<sup>-1</sup>. The Nujol mull suspension technique was applied to exclude the artificial bands from water. The room temperature Raman spectra were measured in back scattering geometry using a Bruker RFS 100 FT-Raman spectrometer. The 1064 nm line of a Nd:YAG laser was used as the excitation source. Signal detection was performed with a LN-Ge (D418-T) detector. Both IR and Raman spectra were recorded with a spectral resolution of 2 cm<sup>-1</sup>.

#### 3. Results and discussion

Figs. 1–3 show the absorption spectra of  $DyCl_3 \cdot GH_2O$ ,  $HoCl_3 \cdot GH_2O$  and  $ErCl_3 \cdot GH_2O$  single crystals at 4.2 K. The band structure is very rich: the spectra consist of many narrow lines with bandwidths of several wavenumbers. It is worth noting that this very rich structure, typical for  $Ln^{3+}$  transitions at low temperatures, is observed even at room temperature (the absorption spectra measured at room temperature are omitted for clarity). The identification of the observed groups of lines both at room temperature and at 4.2 K can be easily achieved by comparison with the calculated energies of the  $Ln^{3+}$  aquo-ions [16,17].

The calculated oscillator strength values (*P*) for the identified transitions are presented in Tables 1–3. The experimental oscillator strength values, determined from the room temperature spectra, are used to estimate the  $\tau_{\lambda}$  intensity parameters (see Tables 1–3). For all the lanthanide chlorides under study, several fittings of  $\tau_{\lambda}$  parameters were performed and the fit was optimised to minimise the root mean square (RMS) deviation, calculated as the radical of the sum of the squares of deviations divided by the difference of the number of transitions considered and the number of parameters. Only the results of the best fits are presented. It is worth noting that errors in the estimation of the parameters  $\tau_{\lambda}$  are small.



Fig. 1. Absorption spectra of the DyCl<sub>3</sub>·6H<sub>2</sub>O crystal measured at 4.2 K.



Fig. 2. Absorption spectra of the HoCl<sub>3</sub>·6H<sub>2</sub>O crystal measured at 4.2 K.



**Fig. 3.** Absorption spectra of the ErCl<sub>3</sub>·6H<sub>2</sub>O crystal measured at 4.2 K.

Intensities of the f–f transitions at room temperature, in particular for hypersensitive transitions, are higher than those usually found for aquo-ions [16,17]. We also observed this relation for the  $\tau_2$  parameter values. This behaviour can be most likely attributed to

#### Table 1

The oscillator strength values  $P\times 10^{-8}$  of f–f transitions at different temperatures and the  $\tau_\lambda\times 10^{-9}$  parameter values at 293 K for the DyCl\_3·6H\_2O crystal,  $C_{Dy}^{3+}$  = 6.128 mol/dm<sup>3</sup>.

Transition: ${}^{6}\text{H}_{15/2} \rightarrow$	Wavelength	<i>P</i> (×10 <sup>8</sup> )	
	(nm)	293 K	4.2 K
<sup>6</sup> H <sub>11/2</sub>	1880-1650	110.64	35.89
<sup>6</sup> H <sub>9/2</sub> , <sup>6</sup> F <sub>11/2</sub>	1407-1190	360.05	170.56
<sup>6</sup> F <sub>9/2</sub> , <sup>6</sup> H <sub>7/2</sub>	1190-1030	237.43	87.05
<sup>6</sup> H <sub>5/2</sub>	1002-969	2.02	2.01
<sup>6</sup> F <sub>7/2</sub>	969-850	255.01	82.81
<sup>6</sup> F <sub>5/2</sub>	850-775	109.34	63.97
<sup>6</sup> F <sub>3/2</sub>	775-740	21.85	8.34
<sup>4</sup> F <sub>9/2</sub>	500-464	16.73	14.53
<sup>4</sup> I <sub>15/2</sub>	464-438	44.75	29.61
${}^{4}G_{11/2}$	438-416	14.77	11.57
${}^{4}F_{7/2}$ , ${}^{4}I_{13/2}$ , ${}^{4}M_{21/2}$ , ${}^{4}K_{17/2}$	416-373	213.95	160.30
${}^{4}M_{19/2}$ , $({}^{4}P, {}^{4}D)_{3/2}$ , ${}^{6}P_{5/2}$ , ${}^{4}I_{11/2}$	373-358	280.87	102.22
<sup>6</sup> P <sub>7/2</sub>	358-343	357.62	161.13
$({}^{4}M, {}^{4}I)_{15/2}, ({}^{4}F, {}^{4}D)_{5/2}, {}^{4}I_{9/2}$	343-333	35.45	17.92
${}^{4}\text{G}_{9/2}, {}^{6}\text{P}_{3/2}, {}^{4}\text{M}_{17/2}$ $({}^{4}\text{G}, {}^{2}\text{F})_{7/2}, {}^{4}\text{K}_{15/2}, {}^{4}\text{D}_{1/2},$	333 -308	210.38	11.74
$({}^{4}\text{D}, {}^{4}\text{G})_{5/2}, {}^{4}\text{L}_{19/2}$			
${}^{4}\text{H}_{13/2}, {}^{4}\text{F}_{3/2}, ({}^{4}\text{K}, {}^{4}\text{L})_{13/2}, {}^{4}\text{D}_{7/2}, {}^{4}\text{H}_{11/2}, {}^{4}\text{G}_{9/2},$	308-283	158.73	
${}^{4}F_{5/2}, {}^{4}G_{11/2}, {}^{4}L_{17/2}$			
( <sup>4</sup> G, <sup>4</sup> H) <sub>7/2</sub>	283-270	37.30	
$({}^{4}G, {}^{4}P)_{5/2}, ({}^{4}P, {}^{4}F)_{3/2}$	263-253	74.25	
$\tau_2 \times 10^9 ({\rm cm})$	2.83 ± 1.06		
$\tau_4 \times 10^9 (\text{cm})$	$3.56 \pm 0.45$		
$\tau_{6} \times 10^{9}  (\text{cm})$	$4.77 \pm 0.48$		
,			

#### Table 2

The oscillator strength values  $P \times 10^{-8}$  of f-f transitions at different temperatures and the  $\tau_\lambda \times 10^{-9}$  parameter values at 293 K for the HoCl<sub>3</sub>·6H<sub>2</sub>O crystal, C<sub>Ho</sub><sup>3+</sup> = 6.142 mol/dm<sup>3</sup>.

Transition: ${}^{5}I_{8} \rightarrow$	Wavelength (nm)	<i>P</i> (×10 <sup>8</sup> )	
		293 K	4.2 K
<sup>5</sup> I <sub>6</sub>	1300-1050	119.82	56.97
<sup>5</sup> I <sub>5</sub>	950-801	22.86	7.36
<sup>5</sup> F <sub>5</sub>	680-600	328.84	281.27
<sup>5</sup> S <sub>2</sub> , <sup>5</sup> F <sub>4</sub>	580-510	451.17	85.90
<sup>5</sup> F <sub>3</sub>	500-478	160.07	42.11
<sup>5</sup> F <sub>2</sub>	478-463	125.22	42.46
<sup>3</sup> K <sub>8</sub>			+41.28
<sup>5</sup> G <sub>6</sub> , <sup>5</sup> F <sub>1</sub>	463-428	1304.99	411.71
( <sup>5</sup> G, <sup>3</sup> G) <sub>5</sub>	430-400	333.66	138.88
<sup>5</sup> G <sub>4</sub> , <sup>3</sup> K <sub>7</sub>	400-376	126.36	88.12
( <sup>5</sup> G, <sup>3</sup> H) <sub>5</sub> , <sup>3</sup> H <sub>6</sub> , ( <sup>5</sup> F, <sup>3</sup> F, <sup>5</sup> G) <sub>2</sub>	371-349	532.94	292.09
<sup>5</sup> G <sub>3</sub> , <sup>3</sup> L <sub>9</sub>	349-339	76.86	
$({}^{3}F, {}^{3}H, {}^{3}G)_{4}, {}^{3}K_{6}$	339-328	87.51	
<sup>5</sup> G <sub>2</sub>	328-314	18.23	
$ au_2  imes 10^9 \ (cm)$	$3.90 \pm 0.48$		
$\tau_4 \times 10^9  (cm)$	$4.56 \pm 0.71$		
$\tau_6 \times 10^9 \text{ (cm)}$	$3.32 \pm 0.47$		

#### Table 3

The oscillator strength values  $P\times10^{-8}$  of f–f transitions at different temperatures and the  $\tau_\lambda\times10^{-9}$  parameter values at 293 K for the ErCl<sub>3</sub>·6H<sub>2</sub>O crystal, C<sub>Er</sub><sup>3+</sup> = 6.157 mol/dm<sup>3</sup>.

Transition: ${}^{4}I_{15/2} \rightarrow$	Wavelength (nm)	P (×10 <sup>8</sup> )	
		293 K	4.2 K
<sup>4</sup> I <sub>13/2</sub>	1700-1300	403.42	
${}^{4}I_{11/2}$	1040-925	59.39	43.15
<sup>4</sup> I <sub>9/2</sub>	830-776	36.14	29.00
<sup>4</sup> F <sub>9/2</sub>	700-590	194.56	99.49
<sup>4</sup> S <sub>3/2</sub>	570-536	44.09	69.99
$^{2}H_{11/2}$	536-500	407.61	249.50
		441.74 <sup>200K</sup>	
<sup>4</sup> F <sub>7/2</sub>	506-470	157.89	76.50
,		208.40 <sup>200K</sup>	
<sup>4</sup> F <sub>5/2</sub> , <sup>4</sup> F <sub>3/2</sub>	470-421	1124.24	
( <sup>2</sup> G, <sup>4</sup> F, <sup>2</sup> H) <sub>9/2</sub>	421-399	69.38	
<sup>4</sup> G <sub>11/2</sub>	399-371	793.66	385.01
		801.02 <sup>200K</sup>	
<sup>4</sup> G <sub>9/2</sub>	371-361	162.88	122.85
$^{2}K_{15/2}$ , $^{2}G_{7/2}$	361-353	89.45	73.11
$({}^{2}P, {}^{2}D, {}^{4}F)_{3/2}$	317-311	5.72	
<sup>2</sup> K <sub>13/2</sub> , <sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> P <sub>1/2</sub>	306-297	16.75	
<sup>4</sup> G <sub>7/2</sub>	297-290	34.24	
( <sup>2</sup> H, <sup>2</sup> G) <sub>9/2</sub>	278-271	45.31	
<sup>2</sup> D <sub>5/2</sub>	260-259	7.49	
<sup>2</sup> D <sub>5/2</sub> , <sup>4</sup> D <sub>7/2</sub>	259-250	1012.64	
${}^{2}I_{11/2}$ , ${}^{2}L_{17/2}$	245-238	131.61	
$^{4}D_{3/2}$ , $(^{2}D, ^{2}P)_{3/2}$	238-234	10.61	
<sup>4</sup> I <sub>13/2</sub>	234–227	78.53	
$\tau_2 \times 10^9  (\text{cm})$	2.41 ± 0.52		
$\tau_4 \times 10^9 (\text{cm})$	$4.26 \pm 0.37$		
$\tau_6 \times 10^9 \text{ (cm)}$	$2.20 \pm 0.62$		

the influence of the chloride ions, which can change the first coordination sphere of the lanthanide ions and lead to a decrease in the symmetry of this sphere. Our spectra measured at 4.2 K show the splitting of  $Ln^{3+}$  ion manifolds in the crystal field [18], which confirms that the lanthanide ions occupy low symmetry sites in the crystal structure.

Inspection of Tables 1–3 reveals that the oscillator strength values of the 4f–4f transitions are lower at 4.2 K than at 293 K, especially for the hypersensitive transitions. The same behaviour was observed previously for chlorides and bromides of light lanthanides [6]. It can be attributed to the electron–phonon coupling

and/or the depopulation of the Stark components of the ground state multiplet, and it clearly demonstrates the contribution of the vibronic mechanism to the intensities of the electronic transitions.

The 4.2 K absorption spectra of  $ErCl_3 \cdot 6H_2O$  for  ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$ and  ${}^{4}I_{15/2} \rightarrow {}^{4}G_{11/2}$  hypersensitive transitions as well as the  ${}^{4}I_{15/2} \rightarrow {}^{4}F_{7/2}$  transition show that the number of the observed Stark electronic components is in good agreement with that expected from group theory for one site of  $Er^{3+}$  ions:  $J + \frac{1}{2} = 6$  components for the former two transitions and  $I + \frac{1}{2} = 4$  for the latter one in the case of low symmetry (Fig. 3). This fact is consistent with the X-ray studies for this compound [7,8]. In contrast to the erbium chloride, the number of observed electronic components for  $^5I_8 \rightarrow {}^5G_6$ ,  ${}^5F_1$  hypersensitive transitions of holmium and for  ${}^6H_{15/2} \rightarrow {}^6F_{11/2}$ ,  ${}^6H_{9/2}$  transitions of dysprosium is lower than expected for the single low symmetry site of the Ln<sup>3+</sup> ion (see Figs. 1 and 2). On the other hand, some additional lines with very low intensities coupled with the corresponding electronic lines are observed. They are most likely of vibronic origin. This behaviour is similar to that observed previously for other Ln<sup>3+</sup> systems [19,20]. A vibronic coupling could be responsible for the broadening of the lines and thus for the observation of a smaller number of electronic components for the hypersensitive transitions in the case of the Ho<sup>3+</sup> and Dy<sup>3+</sup> chlorides.

Fig. 2 shows that the low temperature spectra of HoCl<sub>3</sub>·6H<sub>2</sub>O are composed of two groups of components for almost all transitions.

It is especially clearly visible in the region of the  ${}^{5}I_{8} \rightarrow {}^{5}F_{2}$ ,  ${}^{5}I_{8} \rightarrow {}^{5}F_{3}$ and  ${}^{5}I_{8} \rightarrow {}^{3}K_{8}$  transitions, where these groups are separated by 74 cm<sup>-1</sup>. The same behaviour was previously observed for light lanthanide chlorides and bromides [6] in the region of the  ${}^{4}I_{9/2} \rightarrow$  $^{2}P_{1/2}$  (for Nd<sup>3+</sup>) and  $^{3}H_{4} \rightarrow ^{3}P_{0}$  (for Pr<sup>3+</sup>) transitions. However, the separation was larger, being about 100 cm<sup>-1</sup>. This fact suggests that ion-pair interactions occur in the investigated crystals. This kind of interaction has very often been observed for dimers, especially in the case of lanthanide complexes with carboxylic acid [9,12,21] and compounds with halide bridges [6]. It seems that a sufficiently short Ln-Ln distance (about 6 Å) promotes the ion-pair effect. Interaction between rare earth ions in the crystal network is mediated by phonons (for example  $\delta$ (Cl–Ho–Cl)), which are in resonance with the respective splitting of the ground state multiplet. Moreover, hydrogen bonds, which stabilise the structure, may also play a role in this phenomenon.

Vibrational studies of dysprosium, holmium and erbium chlorides were done using infrared absorption and Raman scattering spectroscopy, and these spectra are shown in Figs. 4 and 5. The IR and Raman spectra of Dy(III), Ho(III) and Er(III) chlorides are essentially identical with those of NdCl<sub>3</sub>·6H<sub>2</sub>O, studied by us previously [6]. However, they differ significantly from the spectra of praseodymium chloride [6]. This observation confirms that the crystal structures of dysprosium chloride to erbium chloride are the same as that of neodymium chloride. It means that the compounds investigated in the present study crystallise in the mono-



Fig. 4. The room temperature infrared spectra of Dy(Ho,Er)Cl<sub>3</sub>·6H<sub>2</sub>O crystals in the far-IR (a) and mid-IR (b) regions.



Fig. 5. The room temperature Raman spectra of Dy(Ho,Er)Cl<sub>3</sub>·6H<sub>2</sub>O crystals.

Table 4			
Phonon frequencies (cm <sup>-1</sup> )	of infrared and Raman activ	e modes for the LnCl <sub>3</sub> .6H <sub>2</sub> (	) crystals. Ln = Dy. Ho and Er.

IR			Raman			Assignment
DyCl <sub>3</sub>	HoCl <sub>3</sub>	ErCl <sub>3</sub>	DyCl <sub>3</sub>	HoCl <sub>3</sub>	ErCl <sub>3</sub>	
	3420sh	3534sh	3445sh	3401vs	3408sh	$v_{as,s}(HOH)$ of the coordinated water
3332s,b	3338s,b	3348m,b	3343m	3346vs	3342vs	
3192s,b	3225sh	3176m,b	3247w	3236sh	3243s	
1620vs	1632vs	1614s,b	1649w	1649m	1650s	$\delta$ (HOH) of the coordinated water
	1620s		1630sh	1640sh	1641sh	
			1600sh	1624m	1624s	
1130m,b	1136m,b	1138m,b				γ(H <sub>2</sub> O)
636sh	643sh	654sh	669w	672s	678s	ω(H <sub>2</sub> O)
602s	607s	607s	615w	601s	609s	
480s	490s	479s	570sh		580sh	
			362vw	359m	360m	$v(Ln-OH_2)$
306sh	334m	346w	349w	321m	328m	
	306m	308w		308sh	317sh	
219m	224m	225m	243s	243s	246s	$v_{as}(Ln-Cl)$
213sh	217sh	217sh				
201sh	204sh	204sh	208s	212m	215vs	$\delta(OLnO)$
192m	194m	198m	192sh	196sh	199sh	
162m	162m	163m	169sh	168sh	170sh	$v_{\rm s}({\rm Ln-Cl})$
155sh	155sh	156sh	159s	159s	159vs	
146sh	146sh	144m				$\delta$ (OLnCl) and $\delta$ (ClLnCl)
144m	144m	131m	133m	138s	139s	
130m	133m	119m	125sh	112m	113s	
117m	119m	109m	116m	96m	97s	
108m	109m	104sh	110m			
103sh	104sh	97w	96sh			
97w	97sh					
85w	79sh	85vw		76w	77m	Lattice modes
68vw	61w	68vw				

The notation for the types of the coordinated water molecules vibrations:  $\gamma$  – scissoring,  $\omega$  – wagging;  $v_{as,s}$  – asymmetric and symmetric stretching modes,  $\delta$  – bending modes; relative intensities of the bands: s (strong), m (medium), w (weak), vw (very weak) or sh (shoulder).

clinic symmetry with the P2/n space group and the metal ions occupy f-positions of C<sub>2</sub> symmetry [6-8]. Based on this fact and on factor group analysis, which we performed for [NdX<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]X halides (X = Br, Cl) [6], assignments of the IR and Raman bands were made (Table 4). These systems are built of  $[LnCl_2(H_2O)_6]^+$  isolated polyhedra, where the water molecules serve to stabilise the structure. The vibrations of the water molecules are spread through the whole wavenumber range analysed [22-24]. The stretching and bending vibrations of the coordinated water are observed in the predicted ranges, the former at about 3400 cm<sup>-1</sup> and the latter at about  $1600 \text{ cm}^{-1}$ . The bands at about  $1130 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$ are attributed to  $\gamma(H_2O)$  and  $\omega(H_2O)$  modes, respectively. In the low frequency region, below 600 cm<sup>-1</sup>, it is difficult to distinguish the modes of water molecules and Ln-O or Ln-Cl species. The bands corresponding to the v(Ln–O) stretching modes for the compounds studied are observed in the form of a complex contour at about 290-360 cm<sup>-1</sup>, whereas for Pr chloride they are observed in the region  $230-260 \text{ cm}^{-1}$  [6]. Taking into consideration the Ln-chlorine coordination, with two chlorine ions and six water molecules in the inner sphere of the separate polyhedra, slight changes are observed for the Ln-Cl stretching vibrations in the IR spectra of the compounds studied. These vibrations are observed at 210 and 162  $cm^{-1}$  for Nd [6], 219 and 162  $cm^{-1}$  for Dy, 224 and 162 cm<sup>-1</sup> for Ho, and 225 and 163 cm<sup>-1</sup> for Er. The same tendency is observed in the Raman spectra: the Ln-Cl stretching mode is observed at 216 and 194  $cm^{-1}$  for Nd [6], 243 and 159  $cm^{-1}$  for Dv and Ho, and 246 and 159  $cm^{-1}$  for Er.

As mentioned above, the low temperature absorption spectra show the presence of many weak sideband lines, which arise due to vibronic coupling (Figs. 1–3). Inspection of the IR and Raman spectra of DyCl<sub>3</sub>·6H<sub>2</sub>O, HoCl<sub>3</sub>·6H<sub>2</sub>O and ErCl<sub>3</sub>·6H<sub>2</sub>O single crystals (Figs. 4 and 5) reveals that the energies of some bands correspond well to the weak sideband lines observed in the absorption spectra. This observation allows us to conclude that the Ln–ligand vibrations promote relatively strong vibronic lines, appearing at the displacement frequencies of the localised modes v(Ln-Cl),  $\delta(O-Ln-O)$  and  $\delta(Cl-Ln-O)$ . Our results prove, therefore, the presence of vibronic coupling for the heavy lanthanide chlorides under study, which usually have ionic rather than covalent character.

According to the existing theories of electron–phonon coupling probability, the 4f–4f transitions with  $\Delta J = 0, 2, 4$  should be considered in the analysis of this vibronic coupling [25]. In order to describe this phenomenon quantitatively, the strength of the vibronic coupling was estimated, and deconvolution into electronic and vibronic components was performed for each particular band corresponding to the 4f–4f transitions at 4.2 K using the TAUS program [26]. Then, the sum of the integrated intensities for all observed vibronic sidebands ( $I_{VIB}$ ), the integrated intensity of zero-phonon electron lines ( $I_{0-phonon}$ ) and the  $R = I_{VIB}/I_{0-phonon}$  rates were calculated. The results are presented in Table 5. The estimated R values for the absorption transitions with  $\Delta J = 2$  ( $\mathbf{U}^{(2)} \neq 0$ ) and  $\Delta J = 4$  ( $\mathbf{U}^{(2)} = 0$ ) are different for Dy<sup>3+</sup> and Ho<sup>3+</sup> chlorides. We may, therefore, conclude that the contribution of the  $\Delta$  process to the vibronic intensities observed by Blasse et al. [25]

Table 5	
The $R = I_{\rm VIB}/I_{\rm 0-phonon}$	ratio for Dy(III), Ho(III) and Er(III) chlorides.

	$({f U}^{(2)})$	$\Delta J$	$R = I_{\rm VIB}/I_{\rm 0-phonon}$
Dy <sup>3+</sup> :			
${}^{6}\text{H}_{15/2} \rightarrow {}^{4}\text{F}_{11/2}$	≠0	2	1.08
${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{P}_{7/2}$	= 0	4	0.68
Ho <sup>3+</sup> : ${}^{5}I_{8} \rightarrow {}^{5}G_{6}$	≠0	2	0.68
$\begin{array}{l} Er^{3+}\colon & \\ {}^{4}I_{15/2} \rightarrow {}^{2}H_{11/2} \\ {}^{4}I_{15/2} \rightarrow {}^{4}G_{11/2} \\ {}^{4}I_{15/2} \rightarrow {}^{4}F_{7/2} \end{array}$	≠0 ≠0 =0	2 2 4	1.16 1.07 1.28

can be neglected for these ions. The opposite relation was observed for Er<sup>3+</sup> chloride. The change of the *R* value with the decrease of the Ln<sup>3+</sup> ionic radius (see Table 5) indicates significant differences in the vibronic coupling strength along the lanthanide series in the chlorides studied, but these changes are not monotonic. The fluctuations are the same as those observed for many other systems [27], in spite of the ionic character of the lanthanide chloride crystals, for which the vibronic coupling strength is less than expected for compounds with covalent bonds. For example, de Mello Donega observed R = 0.9 ( ${}^{3}H_{4} \rightarrow {}^{3}P_{0}$ ) for the  $Pr^{3+}$  ion in  $Y_{2}O_{2}S$ :Pr with a covalent bond [25b], while we determined  $R = 0.58 ({}^{3}\text{H}_{4} \rightarrow {}^{3}\text{P}_{0})$ for a  $Pr^{3+}$  ion in the PrCl<sub>3</sub>·7H<sub>2</sub>O crystal [6]. The *R* values can be treated as a quantitative estimation of the vibronic coupling. Thus, the vibronic coupling strength that we observed in lanthanide chloride crystals is rather high for heavier ions such as Dy<sup>3+</sup> and Er<sup>3+</sup> and much lower for  $Pr^{3+}$  and  $Nd^{3+}$  ions (R = 0.41 and 0.99, for the hypersensitive transitions of the latter ions [6]).

#### 4. Conclusions

Ln<sup>3+</sup> ions occupy one low symmetry site in the structure of DyCl<sub>3</sub>·6H<sub>2</sub>O, HoCl<sub>3</sub>·6H<sub>2</sub>O and ErCl<sub>3</sub>·6H<sub>2</sub>O. The number of electronic components observed in the absorption spectra measured at 4.2 K is compatible with that expected for these systems.

Analysis of the low temperature spectra, especially in the region of the  ${}^{5}I_{8} \rightarrow {}^{5}F_{2}$  and  ${}^{5}I_{8} \rightarrow {}^{5}F_{3}$  transitions for HoCl<sub>3</sub>.6H<sub>2</sub>O, indicates the presence of ion-pair interactions. These interactions lead to the presence of two groups of components separated by 74 cm<sup>-1</sup>. The same behaviour was observed previously for chlorides and bromides of light lanthanides [6] in the region of the  ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$  (for Nd<sup>3+</sup>) and  ${}^{3}H_{4} \rightarrow {}^{3}P_{0}$  (for Pr<sup>3+</sup>) transitions, for which two groups of bands separated by about 100 cm<sup>-1</sup> were clearly observed.

The intensity decrease of some transitions with decreasing temperature was observed for the  $\mathrm{Ho}^{3+}$  and  $\mathrm{Er}^{3+}$  ions in the lanthanide chloride crystals. The same behaviour had also been noticed previously for chlorides and bromides of light lanthanides [6], and it was attributed to the electron–phonon coupling and/or depopulation of the Stark components of the ground state multiplet. This fact demonstrates the contribution of the vibronic mechanism to the intensities of electronic transitions. Vibronic components are very clearly seen as sidebands or additional very weak lines in the low temperature absorption spectra. Assignments of particular vibronic components, made using the IR and Raman data, indicate that they correspond mainly to the stretching v(Ln-Cl) and bending  $\delta(O-Ln-O)$  or  $\delta(Cl-Ln-O)$  vibrations. It seems that these low wavenumber modes play an important role in the electron–phonon coupling.

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