LUMINESCENCE OF LANTHANIDE IONS IN HEXACHLOROELPASOLITES

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Luminescence is reported for the ${}^{6}F_{5/2}$ term in Cs₂NaDyCl₆, for which the normalised energy gap is five vibrational quanta. The luminescence from the ${}^{4}G_{7/2}$ term of NdCl₆³⁻ is reassigned, this being the only luminescent term of NdCl₆³⁻ in the visible spectral region. The normalised energy gap between ${}^{4}G_{7/2}$ and ${}^{2}G_{7/2}$ is spanned by five vibrational quanta. For all other lanthanide ions in hexachloroelpasolites luminescence does not occur from terms with energy gaps spanned by fewer than five phonons. Terms with gaps of five or more phonons luminesce unless they are not populated under the experimental excitation conditions or unless they are depopulated in the neat materials by ion-ion cross-relaxations.

1. Introduction

The electronic energy levels of lanthanide (Ln^{3+}) ions in neat or doped hexachloroelpasolites have been the subject of extensive investigations (see refs. [1-8], and references therein) because the site symmetry of Ln^{3+} is exactly octahedral [9,10] and there are no charge-compensation problems [11]. In the simplest theoretical model the crystal field experienced by Ln³⁺ is described by two parameters [1-4,12,13] but a strong term dependence has been found for these [3,12,13] which is apparently not present if two additional parameters [3,14] are included. Although the experimental studies are not as complete as for Ln³⁺ diluted into the lanthanum trihalides [15,16] most of the energy levels below 25000 cm⁻¹ have been determined for Cs₂NaLnCl₆ and some comparisons have been made with the bromo analogues [2,3,5,7,8]. The fluoro- [17,18] and iodoelpasolites [19] have largely been neglected.

The optical properties of $Cs_2NaLnCl_6$ are at present unexploited although the use of hexachloroelpasolites as millimeter wave laser materials was proposed some time ago [20]. Possibilities also exist for four-level laser operations involving vibronic transitions [21]. Efficient energy transfer from Nd³⁺ or Ho³⁺ to Yb³⁺ [7,22], Ho³⁺ to Tm³⁺ [23] and Ho³⁺ or Tm³⁺ to Er³⁺ [13,24] have been reported in doped elpasolites and numerous ion-ion cross-relaxations have been observed in the neat materials. These cross-relaxations are responsible for the infrared to green upconversion in Cs₂Na(Er_{0.2}Yb_{0.4}-Y_{0.4})Cl₆ [25], green to ultraviolet in Cs₂NaErCl₆ [26], and red to blue-green in Cs₂NaHoBr₆ [27]. All of the above properties are determined by the intensity of luminescence from a suitably populated multiplet term of Ln³⁺, the quantum efficiency being influenced by the type of lattice, the nature of the absorption and luminescence transitions involved. temperature, the concentration of Ln^{3+} , and the presence of impurities, traps or defect sites. The aim of this study is to investigate the dominance of the non-radiative over the radiative rate, as a function of the energy gap between terms and to determine which terms of hexachloroelpasolites are likely to luminesce. The crystal-field levels within each term are in thermal equilibrium so that at low temperature the emission occurs from only the lowest level(s).

For the non-radiative decay of Ln^{3+} from level A in a dilute crystal, a relationship has been found [28] between the spontaneous multiphonon transition rate (MPR) to the next lowest term, *B*, and the normalised energy gap ^{#1}, $n = E_{AB}/\bar{\nu}$ (E_{AB} , the energy gap,

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and $\bar{\nu}$, the maximum phonon energy, both being expressed in wavenumbers). For the LaCl₃/LaBr₃ hosts the MPR decreases by a factor close to 30 for an energy gap spanned by n phonons, relative to one spanned by n-1, so that for a low-order phonon process level A is non-luminescent. In section 2.1 we report luminescence from a term in Cs₂NaDyCl₆ for which the normalised gap is only five phonons. For hexachloroelpasolites the highest energy vibrational mode is the Ln-Cl symmetric stretch, the energy varying from 280 to 300 cm⁻¹ for Ln = Ce - Yb. The highest-energy, prominent vibronic origin in the electronic spectra, corresponding to the S_6 longitudinal optic/S₁ zone boundary mode, is at a similar energy. In section 2.2 we show that a previous report of a low-temperature luminescent level in a hexachloroelpasolite exhibiting a normalised energy gap, n, of two phonons is incorrect. This qualitative study of MPR in lanthanide elpasolites precedes quantitative investigations [30] of relaxation rates.

The preparation of neat and doped elpasolites [23] and the experimental apparatus [12,26] have been described previously.

2. Results and discussion

2.1. Luminescence from the ${}^{6}F_{5/2}$ term in $Cs_2NaDyCl_6$

Foster and Richardson have reported the optial spectra of Dy³⁺ in cubic elpasolite hosts [31], identifying one luminescent term, ${}^{4}F_{9/2}$, near 21000 cm⁻¹. Since the normalised energy gap below ${}^{4}F_{9/2}$ is more than twenty phonons the concentration quenching of luminescence [31] is due to a cross-relaxation between Dy³⁺ ions, the ${}^{6}F_{3/2}$ or ${}^{6}F_{5/2}$ and ${}^{6}H_{9/2}$, ${}^{6}F_{11/2}$ levels being populated. From the absorption spectrum of Cs₂NaDyCl₆ (fig. 1) the energy gap between ${}^{6}F_{3/2}$ and ${}^{6}F_{5/2}$ is 760 cm⁻¹ and that between ${}^{6}F_{5/2}$ and ${}^{6}F_{5/2}$

These gaps are spanned by three and five quanta of the highest energy vibration respectively, so that



Fig. 1. ${}^{6}F_{5/2}$, ${}^{6}F_{7/2} \leftarrow {}^{6}H_{15/2}$ absorption spectrum of Cs₂NaDyCl₆ at 25 K. Note: From the vibronic analysis of these transitions, $({}^{6}F_{5/2})\Gamma_7$, Γ_8 are located at 12390, 12489 cm⁻¹, and $({}^{6}F_{7/2})\Gamma_7$, Γ_8 , Γ_6 at 11036, 11079 and 11120 cm⁻¹ respectively, these energies being similar to the values given in ref. [31]. Also note the scale discontinuity.

it was of interest to determine if MPR from ${}^{6}F_{3/2}$ or ${}^{6}F_{5/2}$ dominates the radiative process. Luminescence from ${}^{6}F_{3/2}$ would occur to low energy of 13249 cm⁻¹. This is essentially coincident with the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{9/2}$, ${}^{6}F_{11/2}$ transitions but no additional bands are observed in this region of the 454 nm - excited luminescence spectrum of $DyCl_6^{3-}$. However, some very weak, otherwise unassigned bands are observed in dilute $Cs_2NaGd_{0.99}Dy_{0.01}Cl_6$ below 12392 cm⁻¹. In the 10 K spectrum these are identified with vibronic sidebands of $({}^{6}F_{5/2})\Gamma_{7} \rightarrow \Gamma_{6}$, $a\Gamma_{8}$, $\Gamma_{7}({}^{6}H_{15/2})$ the transitions to the terminal b, $c\Gamma_8$ levels being obscured by ${}^{4}F_{9/2} \rightarrow {}^{6}H_{7/2}$, ${}^{6}F_{9/2}$. The electric-quadrupole-allowed $({}^{6}F_{5/2})\Gamma_{7} \rightarrow \Gamma_{6}({}^{6}H_{15/2})$ and the magnetic-dipole-allowed $({}^{6}F_{5/2})\Gamma_{7} \rightarrow a\Gamma_{8}({}^{6}H_{15/2})$ origins are observed much weaker than the associated vibronic structure. This is as expected for these transitions, but not for emission from a trap or defect site. Luminescence therefore occurs from a term for which the normalised energy gap is spanned by five phonons.

2.2. Luminescence from the ${}^{4}G_{7/2}$ term of NdCl $_{6}^{3-}$

Foster, Richardson and Schwartz have made a study of the complex optical spectra of the f³ ion, Nd³⁺ in the cubic elpasolite Cs₂NaYCl₆. Under 514.5 nm argon-ion excitation luminescence was reported from a level assigned to $({}^{4}G_{7/2})\Gamma_{8}$ (at 18627 cm⁻¹ [32]), and in addition from $({}^{4}D_{3/2})\Gamma_{8}$ (at 27634 cm⁻¹) under near ultraviolet excitation. Observation of luminescence from the latter level may be expected, since the ${}^{4}D_{3/2}{}^{-2}P_{3/2}$ gap is calculated to be 1605–1935 cm⁻¹ [1,32]. However, the $({}^{4}G_{7/2})\Gamma_{8}$

^{#1} At low temperatures the normalised energy gap is similar to the order of the process, P_{AB} , comprising one quantum of the promoting mode and quanta of the accepting mode [29].

 $-\Gamma_{6}({}^{2}K_{13/2})$ gap was calculated [32] to be 385 cm⁻¹ (i.e. only two vibrational quanta). Many unassigned lines just to lower energy of the $({}^{4}G_{7/2})\Gamma_{8} \rightarrow a\Gamma_{8}, \Gamma_{6}, b\Gamma_{8}({}^{4}I_{9/2})$ emission spectrum were attributed to luminescence from the lowest crystal-field multiplet of ${}^{2}K_{13/2}$. Thus Foster et al. proposed that luminescence ocurs from *each* of the two levels of NdCl₆³⁻ separated by two phonons. This was attributed to either (i) separate thermalisation of ${}^{4}G_{7/2}, {}^{2}K_{13/2}$ from ${}^{4}G_{9/2}$ or (ii) slow MPR, but fast radiative decay from ${}^{4}G_{7/2}$.

If luminescence terminates on the electronic ground state from another term just below ${}^{4}G_{7/2}$ then we would expect to observe bands corresponding to the transitions terminating higher electronic levels each to low energy of those from ${}^{4}G_{7/2}$. These are not observed. Furthermore the ${}^{4}G_{9/2} - {}^{4}G_{7/2}$ gap, measured from the absorption spectrum, also spans two vibrational quanta but no luminescence is observed from ${}^{4}G_{9/2}$ at low temperature. We reject hypothesis (ii) and in section 3 we show that MPR dominates the radiative relaxation rate in all cases where levels are separated by two phonons. Luminescence from the upper level may only occur at relatively high temperatures, when it is thermally populated. Thus there appears to be no evidence for hypothesis (i), but in order to convincingly disprove it a complete experimental reinvestigation was undertaken. In this study we show that there is only one luminescent term of Nd^{3+} in the region 19000–17000 cm⁻¹. Since Cs₂NaNdCl₆ is not cubic at liquid helium temperature [10] it is necessary to dilute $NdCl_{6}^{3-}$ into a transparent cubic lattice in order to study its optical spectra. We have employed Cs₂NaGdCl₆ for the host instead of Cs_2NaYCl_6 [32], but the results are analogous.

Fig. 2 shows the 35 K excitation spectrum (monitoring the $({}^{4}F_{3/2})\Gamma_{8} \rightarrow S_{7} + a\Gamma_{8}({}^{4}I_{9/2})$ emission) of Cs₂NaGdCl₆: NdCl₆³⁻ (1 mol%) between 18600 and 19160 cm⁻¹. Analysis of the vibronic structure enables three electronic origins to be located. The $({}^{4}G_{7/2})\Gamma_{8}, \Gamma_{6}, \Gamma_{7}$ levels are assigned at 18629, 18778, 18859 cm⁻¹ respectively, close to the values reported in ref. [32]. No bands are observed in the region between 17543 and 18628 cm⁻¹ so it is unlikely that ${}^{2}K_{13/2}$ lies below ${}^{4}G_{7/2}$. This is supported by a recent calculation [1], in which ${}^{2}K_{13/2}$ is above ${}^{4}G_{7/2}$ (as in the LaCl₃ host [33]), the ${}^{4}G_{7/2}$ - ${}^{2}G_{7/2}$ gap being spanned by five vibrational quanta.



Fig. 2. 35 K excitation spectrum of Cs₂NaGdCl₆: NdCl₆³⁻ between 18600 and 19160 m⁻¹. Note: Some very weak bands correspond to pure magnetic dipole transitions, the remaining features being assigned to vibronic structure of the $({}^{4}G_{7/2})\Gamma_{8}$, Γ_{6} , $\Gamma_{7} \leftarrow a\Gamma_{8}({}^{4}I_{9/2})$ transitions.

We therefore expect (weak) luminescence to occur from ${}^{4}G_{7/2}$, below 18629 cm⁻¹, and fig. 3 shows the 514.5 nm – excited spectrum of $Cs_2NaGdCl_6$: NdCl₆³⁻ (10 mol%) in this region. The $({}^{4}G_{7/2})\Gamma_{8} \rightarrow$ $a\Gamma_8({}^4I_{9/2})$ electronic origin corresponds to the weak band (line 3) at 18629 cm^{-1} , and the origins of transitions to the terminal $({}^{4}I_{9/2})\Gamma_{6}$, b Γ_{8} levels are assigned near 101 and 342 cm^{-1} to lower energy. These values for the ⁴I_{9/2} ground state crystal-field levels are similar to those reported by Foster et al. but differ for the Γ_6 level assigned by Tofield and Weber [34]. Only three bands in fig. 3 remain unassigned (table 1, lines 1, 2 and 15). The relative intensities of these features do not appear to vary greatly with the concentration of Nd in the crystal, but since we cannot locate analogous bands in the excitation spectrum nor associated vibronic structure in luminescence, we do not identify these bands with NdCl₆³⁻ at an octahedral site of symmetry. We conclude that ${}^{4}G_{7/2}$ is the only luminescent term of Nd³⁺ in this spectral region.

When the concentration of Nd in the crystal is reduced below 10 mol% many additional bands appear



Fig. 3. 15 K luminescence spectrum of $Cs_2NaGdCl_6^{3-}$: NdCl_6^3 between 18720 and 17660 cm⁻¹.

of

Table 1

$Cs_2NaGd_{0,9}Nd_{0,1}Cl_6^{a}$					
Line ^{b)}	Wave- number (cm ⁻¹)		Assignment and derived vibrational wavenumber		
			upper level, 4G7/2	lower level, ⁴ I _{9/2}	
1	18661 mw	ſ	T defect sites	٥Γ	
2	18651 mw	l	¹ ₈ , ucleut sites	ar 8	
3	18629 w		Гв	а <i>Г</i> 8	
4	18600 w		Γ_8	$a\Gamma_8$ +ZBac(29)	
5	18588 m		Г	$a\Gamma_8 + S_5(40)$	
6	18571 w		Г	$a\Gamma_8 + S_9(58)$	
7	18554 s		Γ_8	$a\Gamma_8 + S_{10}(75)$	
8	18529 s		Γ_8	$a\Gamma_8 + S_7(100)$	
9	18503 w		Γ_8	$a\Gamma_8 + S_7(126)$	
10	18454 w		Γ_8	$\Gamma_6 + S_{10}(74)$	
11	18443 sh		Γ ₈	$a\Gamma_8 + S_8(186)$	
12	18385 m		Γ_8	$a\Gamma_8 + S_6(244)$	
13	18369 m		Γ_8	$a\Gamma_8 + S_6(260)$	
14	18343 w		Γ	$a\Gamma_8 + S_6(285)$	
15	18324 mw		Γ_8 , defect site	b∏ ₈	
16	18287 mw		Γ	b∏ ₈	
17	18250 bw		Г	$b\Gamma_8 + S_5(37)$	
18	18214 m		Γ_8	$b\Gamma_8 + S_{10}(73)$	
19	18187 mw		Г	$b\Gamma_8 + S_7(100)$	
20	18101 vw		Γ_{8}	$b\Gamma_8 + S_8(186)$	
21	18043 w		Г	$b\Gamma_8 + S_6(244)$	
22	18027 w		Γ_8	$b\Gamma_8 + S_6(260)$	
23	18001 w		Γ ₈	$b\Gamma_8 + S_6(286)$	

514.5 nm excited 15 K luminescence spectrum

^{a)} From the vibronic analysis, the $({}^{4}G_{7/2})\Gamma_{8} \rightarrow a\Gamma_{8}, \Gamma_{6}, b\Gamma_{8}({}^{4}I_{9/2})$ electronic origins are inferred to be at 18629, 18528 and 18287 cm⁻¹ respectively. The notation for the normal modes is that of Lentz [35].

^{b)} See fig. 3.

in the region between 18264 and 17694 cm⁻¹. Similar bands were observed by Foster et al. in $Cs_2NaYCl_6:NdCl_6^{3-}$ (5 mol%) and were responsible for the hypothesis of two luminescent terms of Nd^{3+} . We have identified these bands as the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition of $ErCl_6^{3-}$ [26], which is *strongly* excited by 488 or 514.5 nm argon-ion excitation (fig. 4). We note that the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{13/2}$ transition is observed at lower energy.

3. Summary and conclusions

This study has identified the occurrence of (weak) luminescence from two terms in lanthanide hexa-



Fig. 4. 488 nm excited luminescence spectrum of $Cs_2NaGdCl_6$: $ErCl_6^{3-}$ (1 mol%) between 18300 and 17650 cm⁻¹ at 10 K. Note: These bands are identified in the luminescence of $Cs_2NaGdCl_6^{3-}$ (<10 mol% Nd) and appear due to contamination by trace quantities of Er.

chloroelpasolites which are separated from the next lowest terms by energy gaps spanned by five quanta of the highest energy vibrational mode. From other studies of these compounds there are many instances of terms with energy gaps of four phonons and in all cases these are non-luminescent, as are terms separated by fewer than this number of vibrational quanta. For lanthanide ions diluted into elpasolite host lattices, terms with energy gaps of more than five quanta are luminescent without exception.

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