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Non-resonant energy transfer between Tb^{3+} and Eu^{3+} in the cubic hexachloroelpasolite crystals $Cs_2NaTb_{1-x}Eu_xCl_6$ ($x = 0.01-0.15$)

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Abstract. Luminescence decay curves have been measured for the Eu^{3+} emission and Tb^{3+} emission in the cubic crystals $Cs_2NaTb_{1-x}Eu_xCl_6$ at 80 and 293 K using pulsed dye laser excitation into the 5D_4 state of Tb^{3+} and the 5D_1 state of Eu^{3+} . For excitation of Tb^{3+} , efficient energy transfer occurs to the 5D_0 state (but not the 5D_1 state) of Eu^{3+} and there is fast energy migration within the 5D_3 state. When excitation is into the 5D_1 state of Eu^{3+} , phonon-assisted coupling to the Tb^{3+} ions results in enhanced relaxation to the 5D_0 state but the lifetime of 5D_0 is not affected by the presence of Tb^{3+} . In all cases the non-resonant energy transfer involves creation or annihilation of phonons which have odd parity with respect to the metal centres and cannot be explained within the usual Born–Oppenheimer treatment of phonon-assisted energy transfer. The mechanism of the energy transfer processes is considered in detail.

1. Introduction

Non-radiative energy transfer processes involving trivalent lanthanide ions in inorganic solids have been widely studied in recent years [1] but the majority of the investigations have dealt with Ln^{3+} ions at low-symmetry sites without a centre of inversion. Non-radiative transfer of excitation between Ln^{3+} ions in high-symmetry sites with a centre of inversion should be in principle easier to study and to understand because of the lower number of crystal-field components of the J levels and the small radiative transition probability from the excited states, because the $f \rightarrow f$ electric dipole no-phonon transitions are forbidden.

Cubic crystals of the hexachloroelpasolites $Cs_2NaLnCl_6$ are ideal model systems in which the Ln^{3+} ions occupy perfectly octahedral sites. The excited states of the ions have in general long relaxation times because the $f \rightarrow f$ electric dipole transitions are forbidden and because the multiphonon decay processes are inefficient, owing to the low vibrational frequencies of the crystals. This could lead to possible technological exploitations in the field of optical devices.

Despite the fact that the energy levels of the Ln^{3+} ions in the hexachloroelpasolite crystals are well known [2], investigations of the energy transfer processes in this lattice have been sporadic and have not fully established the nature of the transfer mechanism [3–7].

In this paper we report non-resonant energy transfer from the 5D_4 state of Tb^{3+} to Eu^{3+} and from the 5D_1 state of Eu^{3+} to Tb^{3+} in $Cs_2NaTb_{1-x}Eu_xCl_6$ crystals at 293 and 80 K. The mechanisms of the transfer processes are established and the concentration and temperature dependence of the transfer probabilities are discussed. A preliminary account of part of this study has been reported previously [8].

2. Structural, vibrational and electronic data

$Cs_2NaTbCl_6$, $Cs_2NaEuCl_6$ and Cs_2NaYCl_6 crystallise at room temperature in the $Fm\bar{3}m$ (O_h^5) space group. Each Ln^{3+} ion is surrounded by a perfect octahedron of chloride ions and the closest Ln–Ln distance is about 7.6 Å [9]. The vibrational properties of $Cs_2NaEuCl_6$ have been studied in some detail, giving the three odd vibrations ν_6 , ν_4 and ν_3 of the $EuCl_6^{3-}$ ion as 80 cm^{-1} (ν_6 , τ_{2u}), 102 cm^{-1} (ν_4 , τ_{1u}), 240 cm^{-1} (TO) and 250 cm^{-1} (LO) (ν_3 , τ_{1u}) [10]. Lattice vibrations occur at about 186 cm^{-1} and about 56 cm^{-1} , the former being essentially the Na^+ motion. The vibrational modes of $Cs_2NaTbCl_6$ are very similar [11, 12]. Almost all of the crystal-field terms derived from the 5D and 7F Russell–Saunders terms have been located and the agreement between the experimental and calculated energy levels is good [2].

3. Experimental details

Good-quality crystals of stoichiometries $Cs_2NaTb_{1-x}Eu_xCl_6$ ($x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10$ and 0.15), $Cs_2NaY_{1-x}Tb_xCl_6$ and $Cs_2NaY_{1-x}Eu_xCl_6$ ($x = 0.01, 0.05, 0.10$ and 1.00) were grown in evacuated quartz ampoules by the Bridgman method at 850°C . The crystals were stored over $Mg(ClO_4)_2$ after a careful coating with high vacuum grease in order to reduce to a minimum their exposure to atmospheric water. Absorption and luminescence spectra were measured as previously described [13, 14].

Decay curves of the luminescence were measured by exciting the crystals at 488.0 and 526.0 nm with a Spectron SL2Q + SL3A Nd-YAG laser pumping Coumarin 500 in a Spectron SL4000 dye laser. The duration of the pulses was less than 10 ns. The luminescence was measured at various wavelengths using a Spex Minimate monochromator. The signals were averaged over about 1000 pulses with a modified PARTDH-9 waveform educator (calibrated and tested following the recommendations of the manufacturer) and transferred to a BBC microcomputer. The experimental decay curves were fitted to various theoretical models using a non-linear least squares simplex procedure.

The reproducibility of the decay curves was checked by measuring the luminescence from crystals originating from different preparations for each composition. No radiation-trapping effects could be detected.

All the measurements were performed at 293 and 80 K. The crystals were maintained under vacuum in a simple laboratory-built cryostat.

4. Results and discussion

4.1. Energy transfer from the 5D_4 state of Tb^{3+}

A schematic diagram of the energy levels of Eu^{3+} and Tb^{3+} in $Cs_2NaLnCl_6$ up to $25\,000\text{ cm}^{-1}$ [10–12] is shown in figure 1. Excitation of $Cs_2NaTb_{1-x}Eu_xCl_6$ crystals at 293

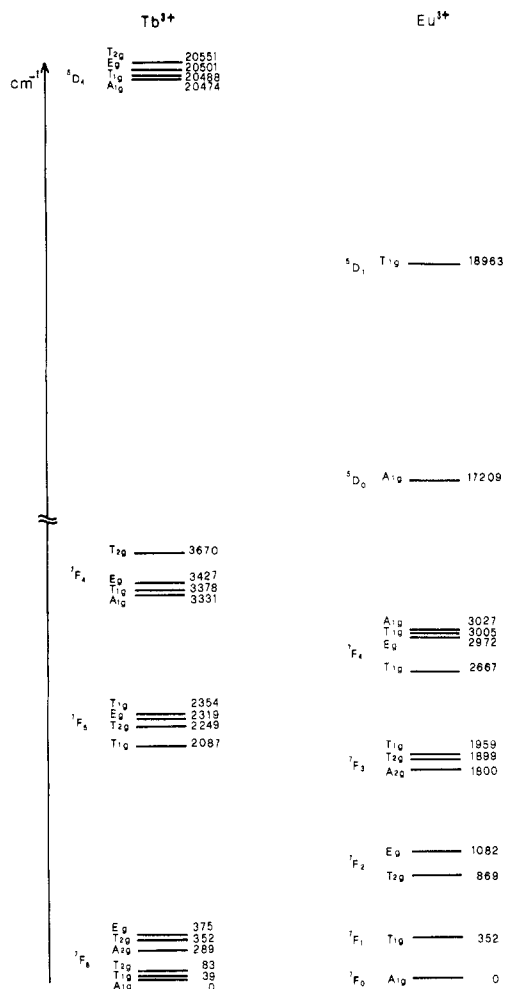


Figure 1. Energy levels for Eu^{3+} and Tb^{3+} in $\text{Cs}_2\text{NaLnCl}_6$ up to $25\,000\text{ cm}^{-1}$.

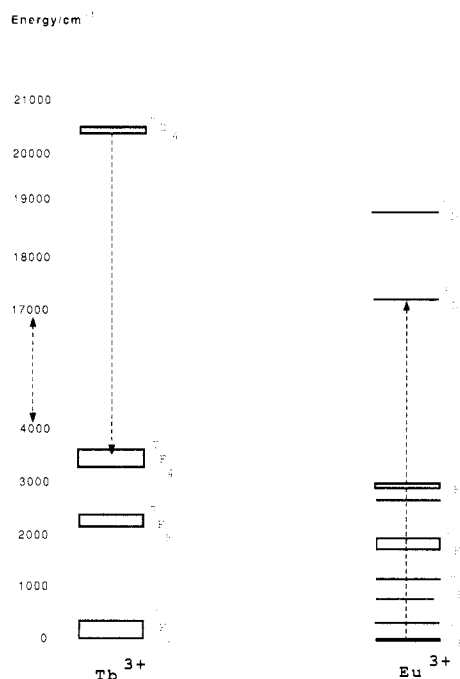


Figure 2. Schematic of the $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer.

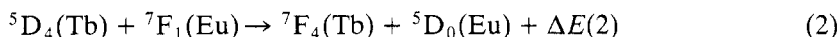
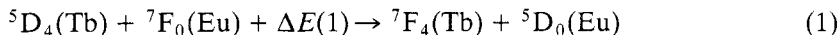
and 80 K using 488.0 nm ($20\,492\text{ cm}^{-1}$) radiation results in intense emission from both the $\text{Tb}^{3+} ^5\text{D}_4$ state and the $\text{Eu}^{3+} ^5\text{D}_0$ state. The $^5\text{D}_4 \rightarrow ^7\text{F}_0$ ($J = 0 \rightarrow 6$) and $^5\text{D}_0 \rightarrow ^7\text{F}_0$ ($J = 1 \rightarrow 5$) transitions are closely similar to those observed for the pure $\text{Cs}_2\text{NaTbCl}_6$ [11, 12] and $\text{Cs}_2\text{NaEuCl}_6$ [10] but, whilst the former is strongly excited by the 488.0 nm excitation, very little emission from $\text{Cs}_2\text{NaEuCl}_6$ or $\text{Cs}_2\text{NaY}_{1-x}\text{Eu}_x\text{Cl}_6$ is produced by excitation at this wavelength. Significantly no luminescence from the $\text{Eu}^{3+} ^5\text{D}_1$ state could be detected in the 488.0 nm excited luminescence spectrum of $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$. The excitation is therefore non-radiatively transferred from $^5\text{D}_4$ of Tb^{3+} to the Eu^{3+} ion directly either to the $^5\text{D}_0$ state or to the $^5\text{D}_1$ state, which relaxes so rapidly to the lower-lying $^5\text{D}_0$ state that no emission is observed. These alternatives may be distinguished since direct excitation at 527.3 nm in the $^5\text{D}_1$ level of Eu^{3+} in $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$ (see section 4.2) gives an intense luminescence spectrum from the same $^5\text{D}_1$ level, which decays with a decay rate at 293 K of $(4.2 \pm 0.2) \times 10^4\text{ s}^{-1}$ and at 80 K of $(7.8 \pm 0.4) \times 10^2\text{ s}^{-1}$. The excitation is therefore transferred directly to $^5\text{D}_0$ after pumping in the $^5\text{D}_4$ state of Tb^{3+} .

Figure 1 shows that no resonant energy transfer process from the $^5\text{D}_4$ state of Tb^{3+}

Table 1. Decay rate constants of the 5D_4 state of Tb^{3+} and rise rate constants of the 5D_0 state of Eu^{3+} in the $Cs_2NaTb_{1-x}Eu_xCl_6$ crystals at 293 and 80 K.

x	k ($10^2 s^{-1}$)			
	Decay 5D_4		Rise 5D_0	
	293 K	80 K	293 K	80 K
0	1.51	1.06	—	—
0.01	1.66	1.12	—	—
0.02	1.87	1.23	—	—
0.03	2.45	1.50	3.04	1.89
0.04	3.42	2.16	3.56	2.13
0.05	3.34	1.92	3.52	1.92
0.07	4.65	2.56	4.66	2.54
0.10	6.35	3.34	6.67	3.13
0.15	11.57	4.57	11.71	3.59

to 5D_0 of Eu^{3+} can occur. The most probable mechanisms responsible for the direct transfer of excitation are [8, 15] (figure 2)



where the energy mismatches $\Delta E(1)$ and $\Delta E(2)$ can be bridged respectively by the absorption or the emission of the phonons or by the involvement of energy levels of other ions in a many-body process. Further information about the mechanism responsible for the transfer can be obtained from the analysis of the kinetics of the luminescence as a function of the fractional concentration x and of the temperature.

For the diluted $Cs_2NaY_{1-x}Tb_xCl_6$ and the pure $Cs_2NaTbCl_6$ crystals the decay curves of the luminescence from the 5D_4 level, excited at 488.0 nm and detected at 548.0 nm, i.e. in the $^5D_4 \rightarrow ^7F_5$ transition, are exactly exponential for more than six half-lives at 293 and 80 K. The decay constant k is $(1.45 \pm 0.04) \times 10^2 s^{-1}$ at 293 K and $(1.01 \pm 0.04) \times 10^2 s^{-1}$ at 80 K for $x = 0.01$, very slightly increasing to $(1.51 \pm 0.03) \times 10^2 s^{-1}$ at 293 K and $(1.06 \pm 0.02) \times 10^2 s^{-1}$ at 80 K for $Cs_2NaTbCl_6$. The differences between the decay rates for the most diluted $Cs_2NaY_{1-x}Tb_xCl_6$ mixed crystals and the pure Tb^{3+} elpasolite are comparable with experimental uncertainties so that the luminescence from the 5D_4 state is not self-quenched in this lattice in the temperature range under examination. This is not surprising since examination of figure 1 shows that there are no three ion combinations that allow efficient relaxation.

The decay curves of the luminescence from 5D_4 for all the $Cs_2NaTb_{1-x}Eu_xCl_6$ crystals are again exactly exponential for more than six half-lives at both 293 and 80 K (figure 3). The values of the decay rates k extracted from the experimental decay curves are higher than those obtained for the pure Tb^{3+} elpasolite and therefore the Eu^{3+} ion quenches the Tb^{3+} luminescence (table 1). The exact exponential shape of the decay curves demonstrates that the energy transfer process is preceded by a fast resonant migration among the donors [16], as expected owing to the high concentration of the Tb^{3+} ions in the lattice. In the presence of fast migration, the transfer process can be described using a rate equation approach [17, 18] and the decay curve is expressed by

$$\varphi(t) = A \exp[-(k_D^0 + k_{ET})t] \quad (3)$$

where k_D^0 is the internal decay rate of the donor and k_{ET} is the energy transfer probability.

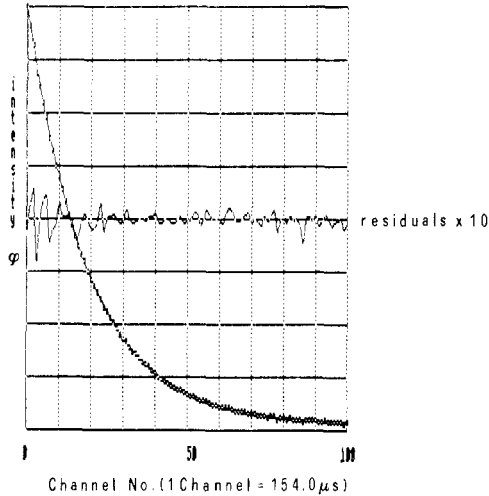


Figure 3. Time evolution of the luminescence from the $^5\text{D}_4$ state of Tb^{3+} in $\text{Cs}_2\text{NaTb}_{0.95}\text{Eu}_{0.05}\text{Cl}_6$ ($\lambda_{\text{exc}} = 488.0$ nm, $\lambda_{\text{obs}} = 548.0$ nm) at 293 K: \cdots , experimental data; —, fit to equation (3). The residuals of the fit are also shown.

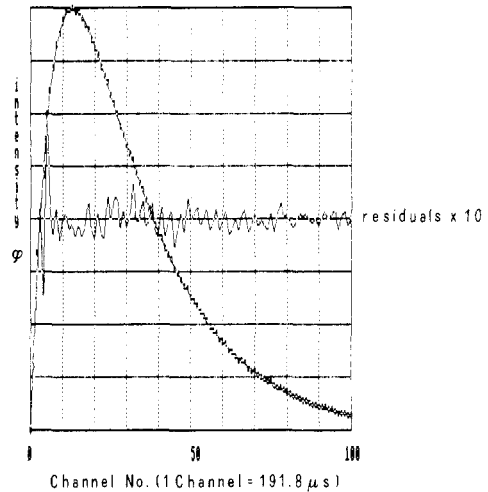


Figure 4. Time evolution of the luminescence from the $^5\text{D}_0$ state of Eu^{3+} in $\text{Cs}_2\text{NaTb}_{0.90}\text{Eu}_{0.10}\text{Cl}_6$ ($\lambda_{\text{exc}} = 488.0$ nm, $\lambda_{\text{obs}} = 593.0$ nm) at 293 K: \cdots , experimental data; —, fit to equation (4). The residuals of the fit are also shown.

Following the rate equation approach, k_{ET} depends on the concentrations of the donor and acceptor in a way that reflects the number of ions involved in the process.

No direct information concerning the energy migration can be obtained from these experimental data [16]. The resonant energy migration would involve transitions connecting the lowest crystal-field components of the $^5\text{D}_4$ and the $^7\text{F}_6$ states. These transitions are formally electric quadrupole allowed and therefore the fact that fast migration is present at 80 K agrees with a quadrupole–quadrupole mechanism, which is temperature independent, whereas resonant migration involving an electric dipole–electric dipole mechanisms would require the excitation of ungerade phonons in this lattice and would be temperature dependent.

The luminescence from the $^5\text{D}_0$ state of Eu^{3+} , after excitation of the $^5\text{D}_4$ state of Tb^{3+} , shows a distinct rise from zero intensity followed by a slower decay at both 293 and 80 K (figure 4). The experimental dependence of the emission intensity $\varphi(t)$ on time is very well fitted (for $0.03 \leq x \leq 0.15$) by an equation of the type

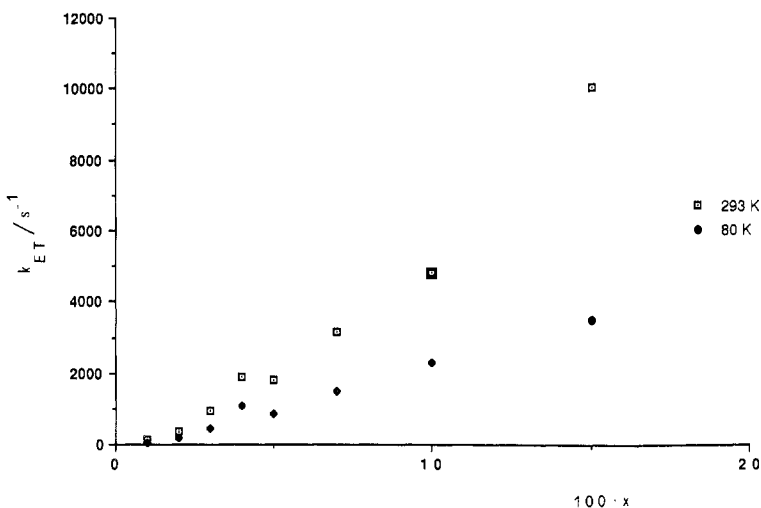
$$\varphi(t) = B[\exp(-k_1 t) - \exp(-k_2 t)] \quad (4)$$

where k_1 corresponds to the decay rate of the $^5\text{D}_0$ state for $\text{Cs}_2\text{NaY}_{1-x}\text{Eu}_x\text{Cl}_6$ ($0.01 \leq x \leq 0.10$) after $^5\text{D}_1$ excitation ($k_1 = 1.9 \times 10^2 \text{ s}^{-1}$ at 293 K and $k_1 = 9.5 \times 10^1 \text{ s}^{-1}$ at 80 K [19] and k_2 is experimentally identical with the total decay rate for Tb^{3+} in the same conditions and at 293 and 80 K (table 1). For $x < 0.03$ the emission intensity from $^5\text{D}_0$ after $^5\text{D}_4$ excitation is too weak to allow detailed analysis. The experimental results agree with the solution of a rate equation describing the transfer from the ‘short-lived’ $^5\text{D}_4$ state to the ‘long-lived’ $^5\text{D}_0$ state, in the presence of fast migration of the excitation among the Tb^{3+} donors. These results confirm the conclusions drawn above.

The values of k_{ET} at 293 and 80 K deduced from the decay curves of $^5\text{D}_4$ for the $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$ crystals by taking $k_{\text{D}}(293 \text{ K}) = 1.51 \times 10^2 \text{ s}^{-1}$ and $k_{\text{D}}(80 \text{ K}) = 1.06 \times 10^2 \text{ s}^{-1}$ are given in table 2. We estimate that the experimental uncertainty of the values of k_{ET} is approximately $\pm 15\%$. The dependence of k_{ET} at 293 and 80 K upon the

Table 2. Energy transfer rates k_{ET} from the 5D_4 state of Tb^{3+} in $Cs_2NaTb_{1-x}Eu_xCl_6$ crystals at 293 and 80 K.

x	$k_{ET} (10^2 s^{-1})$	
	293 K	80 K
0.01	0.15	0.06
0.02	0.36	0.17
0.03	0.94	0.44
0.04	1.91	1.10
0.05	1.83	0.86
0.07	3.14	1.50
0.10	4.84	2.28
0.15	10.06	3.51

**Figure 5.** Dependence of the energy transfer probability k_{ET} from the 5D_4 state of Tb^{3+} to the 5D_0 state of Eu^{3+} in $Cs_2NaTb_{1-x}Eu_xCl_6$ upon the fractional concentration x at 293 and 80 K.

fractional concentration x is shown in figure 5. k_{ET} increases approximately in a linear way with increasing concentration of Eu^{3+} at both 293 and 80 K over the range of concentrations considered, with some evidence of a deviation towards a higher power dependence for $x > 0.10$ at 293 K. This linear dependence shows that, in the energy transfer process, only one Eu^{3+} ion is involved [17] and therefore that the energy transfer process is phonon assisted for low fractional concentration of Eu^{3+} . The ratio $(k_{ET}(293\text{ K})/k_{ET}(80\text{ K}))$ of the energy transfer probabilities at 293 and 80 K is roughly constant for $0.01 \leq x \leq 0.10$ and its average value is 2.1 ± 0.2 .

The energy transfer processes (1) and (2) formally involve the electronic absorption transitions $^7F_0 \rightarrow ^5D_0$ and $^7F_1 \rightarrow ^5D_0$ on the Eu^{3+} centres. The former electronic transition is highly forbidden and its intensity is usually very low [20]. On the other hand, the latter transition is purely magnetic dipole allowed, and it is well known that couplings formally involving magnetic dipole transitions give rise to negligible energy transfer probabilities [21]. Moreover, the 7F_1 state of Eu^{3+} lies 352 cm^{-1} above the ground state

in the hexachloroelpasolite lattice (figure 1) and a transfer process such as (2) would be strongly temperature dependent, as the predicted ratio $k_{\text{ET}}(293 \text{ K})/k_{\text{ET}}(80 \text{ K})$ would be higher than 60. Mechanisms (2) alone therefore cannot account for the observed energy transfer rates.

We assign the transfer mechanism as a combination of process (1) and (2), but we emphasise that the contribution of (2) is likely to be almost negligible. On the other hand, mechanisms (1) formally involves the ${}^7\text{F}_0 \leftrightarrow {}^5\text{D}_0$ transition of EuCl_6^{3-} . This transition is electric dipole, electric quadrupole and magnetic dipole forbidden in an O_h crystal field and has never been observed using absorption and luminescence spectroscopy [10, 22]. Recently we have shown that this transition can be easily detected in $\text{Cs}_2\text{NaY}_{1-x}\text{Eu}_x\text{Cl}_6$ ($x = 0.01\text{--}0.10$) and $\text{Cs}_2\text{NaEuCl}_6$ by excitation spectroscopy and that the main spectral features at 12 K are vibronic origins enabled by the ν_4 , ν_3 and sodium lattice vibrations [23]. At 80 and 293 K, hot vibronic origins due to the population of the ν_4 , ν_3 and sodium lattice modes in the electronic ground state are relatively strong. Several of these hot bands in the 80 K ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ excitation spectrum of EuCl_6^{3-} strongly overlap with features in the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ emission spectrum of $\text{Cs}_2\text{NaTbCl}_6$ and $\text{Cs}_2\text{NaYCl}_6 \cdot \text{TbCl}_6^{3-}$ [11]. In particular the hot band at $17\,097 \text{ cm}^{-1}$ due to the TO component of the ν_4 vibronic origin in the 80 K ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ spectrum is almost exactly coincident with the strong feature at $17\,095 \text{ cm}^{-1}$ in the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ spectrum at the same temperature and the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ hot vibronic origin due to the sodium motion vibration at $17\,021 \text{ cm}^{-1}$ lies at the same wavenumber as a sharp band in the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ spectrum. At 293 K, the weakly structured hot high-energy tail of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ overlaps almost completely the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ excitation transition.

These spectral overlaps could help in the precise identification of the electronic transitions and the phonons involved in the energy transfer process. Making use of the assignments of [11], several phonon-assisted energy transfer involving different crystal-field components of ${}^5\text{D}_4$ and different phonons can be predicted. However, the calculation of the temperature dependence of their probability fails to reproduce the observed ratio $k_{\text{ET}}(293 \text{ K})/k_{\text{ET}}(80 \text{ K})$. No single process is therefore dominant and the actual process is probably due to a superposition of several transfers between individual crystal-field states. The detailed determination of the transfer mechanism clearly requires a more complete study of the temperature dependence of the energy transfer and a more reliable assignment of the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ transition [24, 25].

Since the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ no-phonon transition of Eu^{3+} is strictly forbidden, we emphasise that the transfer mechanism (1) must involve the coupling of an electric dipole vibronic transition on the Eu^{3+} centre to an electric quadrupole or electric dipole vibronic transition on the Tb^{3+} centre. As before, we neglect coupling involving magnetic dipole transitions. The electronic origins of the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ transition are, in the intermediate-coupling scheme, magnetic dipole or electric quadrupole allowed.

We note that the phonon-assisted energy transfer process implies in both cases the emission or the absorption of ungerade phonons in a centrosymmetric geometry. This process is forbidden by parity selection rules in the crude adiabatic approximation scheme, whereas its probability becomes different from zero if the vibronic wavefunctions for the energy levels of the donor and the acceptor ions are expressed in the Herzberg–Teller coupling scheme. This argument will be treated in detail elsewhere [26].

The dependence of the energy transfer rates for $x \leq 0.15$ could also be qualitatively explained in terms of many-body processes involving the transfer of excitation from one Tb^{3+} ion in the ${}^5\text{D}_4$ state to one (or more than one) Tb^{3+} ion in the ${}^7\text{F}_6$ state and one Eu^{3+}

ion in the 7F_0 state, without the assistance of phonons. Several of these processes are possible in terms of energy conservation, but the very low oscillator strength of the ${}^7F_0 \rightarrow {}^5D_0$ pure electronic transition makes them extremely unlikely.

4.2. Energy transfer from the 5D_1 state of Eu^{3+}

The decay curves of the luminescence from the 5D_1 state of Eu^{3+} in the $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$ ($x = 0.01\text{--}0.15$) crystals after excitation at 527.3 nm (in the ${}^7F_0 \rightarrow {}^5D_1$ absorption transition) and with observation wavelength equal to 559.8 nm (in the ${}^5D_1 \rightarrow {}^7F_2$ emission transition) are exactly exponential for more than six half-lives for all the compositions and at both 293 and 80 K. The decay rates of the luminescence extracted from the exponential fitting are approximately independent of the fractional concentration x . The average value of k at 293 K is $(4.2 \pm 0.2) \times 10^4 \text{ s}^{-1}$, decreasing to $(7.8 \pm 0.4) \times 10^2 \text{ s}^{-1}$ at 80 K. For comparison, the decay curve of the 5D_1 state in $\text{Cs}_2\text{NaY}_{0.99}\text{Eu}_{0.01}\text{Cl}_6$ is not exactly exponential at 293 K, owing to energy transfer processes, but the decay rate of the isolated 5D_1 can be evaluated as $1.98 \times 10^2 \text{ s}^{-1}$, whereas at 80 K the decay curve is exponential with $k = (1.36 \pm 0.01) \times 10^2 \text{ s}^{-1}$. For the pure crystal $\text{Cs}_2\text{NaEuCl}_6$ the decay curve of 5D_1 is exponential, with decay rate $k = (1.52 \pm 0.08) \times 10^4 \text{ s}^{-1}$ at 293 K and $k = (1.9 \pm 0.1) \times 10^3 \text{ s}^{-1}$ at 80 K [19]. From the experimental results, it is clear that energy transfer processes quench the luminescence from 5D_1 in both the $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$ and the $\text{Cs}_2\text{NaY}_{1-x}\text{Eu}_x\text{Cl}_6$ systems. This is not surprising since examination of figure 1 shows that there are three ion combinations that allow efficient relaxation from 5D_1 .

The efficiency η_T of the energy transfer can be evaluated from the equation [3]

$$\eta_T = 1 - k_D^0/k_D$$

where k_D^0 is the decay rate of the isolated donor and k_D is the decay rate of the donor in the presence of the acceptor. For the $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$ crystals, the efficiencies of the energy transfer from 5D_1 are $\eta_T = 0.995$ at 293 K and $\eta_T = 0.826$ at 80 K. It is therefore evident that energy transfer processes are very efficient in quenching the luminescence from 5D_1 , and much more probable than the energy transfers from the 5D_4 state of Tb^{3+} to the Eu^{3+} ion [8].

The exactly exponential decay curves of 5D_1 in $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$ ($x = 0.01\text{--}0.15$) agree with a relatively slow energy transfer process in presence of a fast migration of the excitation among the Tb^{3+} acceptors [17, 18], as it is reasonable to expect in view of the stoichiometry of the crystals. The process can therefore be described by a rate equation approach and the decay curve is expressed by equation (3), in agreement with the experiment. In all cases the rise rate constant of the 5D_0 emission was similar to the decay constant of the 5D_1 emission.

From equation (3), it is possible to calculate the energy transfer rates k_{ET} and these are found to be approximately independent of x . Assuming that $k_D^0 = 1.98 \times 10^2 \text{ s}^{-1}$ at 293 K and $k_D^0 = 1.36 \times 10^2 \text{ s}^{-1}$ at 80 K, the energy transfer rate for the $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$ crystals is about $k_{ET} = (4.2 \pm 0.2) \times 10^4 \text{ s}^{-1}$ at 293 K and $k_{ET} = (6.4 \pm 0.4) \times 10^2 \text{ s}^{-1}$ at 80 K. The ratio $k_{ET}(293 \text{ K})/k_{ET}(80 \text{ K})$ is about 65. Again, we estimate that the uncertainties of the individual values of k_{ET} are $\pm 15\%$.

Inspection of the energy level diagram in figure 1 shows that the energy transfer from the 5D_1 state of Eu^{3+} to the Tb^{3+} ion is not resonant. Therefore the process either is phonon assisted or involves more than one Tb^{3+} ion. From the energy level diagram, it is possible to predict several phonon-assisted processes conserving the total energy

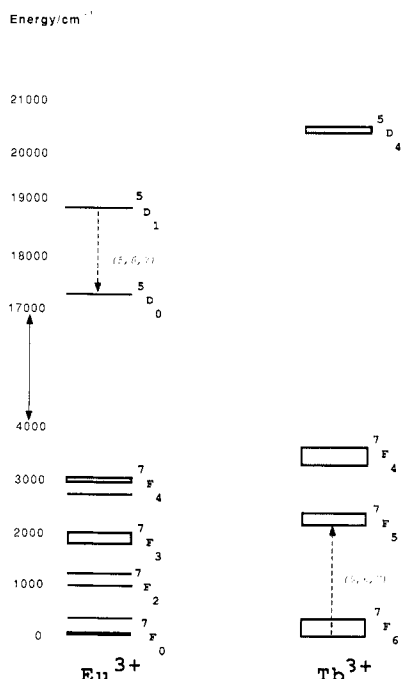
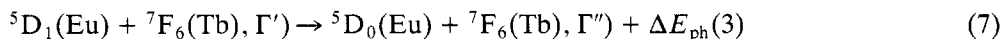
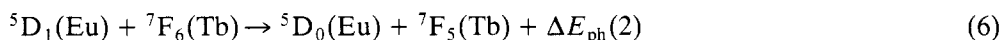
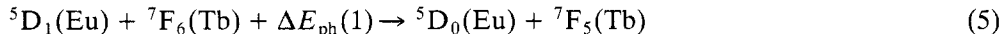


Figure 6. Schematic diagram of the $\text{Eu}^{3+} {}^5\text{D}_1$ relaxation.

of the system. The three most probable (i.e. with the smallest energy mismatches) mechanisms are (figure 6).



where $\Delta E_{\text{ph}}(1) = 40\text{--}600 \text{ cm}^{-1}$, $\Delta E_{\text{ph}}(2) = 20\text{--}40 \text{ cm}^{-1}$ and $\Delta E_{\text{ph}}(3) = 1380\text{--}2120 \text{ cm}^{-1}$; Γ' and Γ'' are the irreducible representations of O_h labelling the crystal-field components of ${}^7\text{F}_6$. Energy transfer processes from Eu^{3+} to Eu^{3+} are also possible [19] but are not considered here owing to the low concentration of Eu^{3+} and the high concentration of Tb^{3+} .

Processes (5)–(7) actually indicate a variety of mechanisms involving different individual crystal-field components of ${}^7\text{F}_6$ and ${}^7\text{F}_5$ and different combination of phonons on the Eu^{3+} and the Tb^{3+} centres. Clearly the problem is very complicated and its solution requires a much more detailed study of the dependence of the energy transfer probability upon the temperature. Moreover, the system is concentrated in the Tb^{3+} ions and there are several many-body processes, involving the transfer of the excitation from one Eu^{3+} ion to two or more Tb^{3+} ions, which satisfy the energy conservation requirements. We note that either phonon-assisted or many-body processes imply only a weak dependence upon the fractional concentration of Tb^{3+} (for $\text{Cs}_2\text{NaTb}_{1-x}\text{Eu}_x\text{Cl}_6$, $x = 0.01\text{--}0.15$) and therefore are in substantial agreement with the experimental results.

Finally, we point out that the processes (5)–(7) formally involve the electronic transition ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$, which is purely magnetic dipole allowed. Owing to the weakness of the energy transfers involving magnetic dipole transitions, we assign the process to the coupling of electric dipole vibronic transitions on the Eu^{3+} centre with electric dipole vibronic or electric quadrupole electronic transitions on the Tb^{3+} centre, in an O_h crystal

field. As in the case of the energy transfer from 5D_4 , these processes are allowed only in the Herzberg–Teller coupling scheme (see section 4.1).

5. Conclusions

We have shown that energy transfer from the 5D_4 state of Tb^{3+} to the 5D_0 state of Eu^{3+} in $Cs_2NaTb_{1-x}Eu_xCl_6$ involves the participation of one or more odd-parity phonons. Similarly, odd phonons are required in the 5D_1 to 5D_0 relaxation of Eu^{3+} in this material. As far as we are aware, this is the first quantitative demonstration of the mechanism of energy transfer involving centrosymmetric lanthanide ions. The use of vibronic wavefunctions is necessary to account for the observed processes.

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