Energy transfer from the $^5D_1$ state of $Cs_2NaY_{1-x}Eu_xCl_6$ and $Cs_2NaEuCl_6$

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Abstract. The luminescence decay curves from the $^5D_1$ state of the cubic hexa-chloroelpasolite crystals $Cs_2NaY_{1-x}Eu_xCl_6$ ($x = 0.01, 0.05, 0.10, 1$) have been measured over the temperature range 12–293 K. For $x = 0.01$, cross-relaxation processes involving odd parity phonons occur at 293 K but are quenched at 80 K. For $x = 0.05$ and 0.10 both temperature-dependent energy migration among the donors and cross-relaxation occur. For the pure material energy transfer from the donors to the nearest-neighbour acceptors becomes dominant and the emission is strongly quenched. The multipole nature of the coupling mechanisms and the identity of the states involved is discussed.

1. Introduction

The non-radiative energy transfer processes involving lanthanide ions in inorganic solids are of considerable technological and scientific interest. Competition between these processes and the radiative and non-radiative relaxation determines the efficiency and spectral output of commercial phosphors. The great majority of detailed studies have investigated the dynamics of the luminescence of lanthanide ions at low symmetry sites in crystals such as LaF_3 [1]. In these cases the f^n manifold generates a large number of crystal field states and the phonon spectrum is complex and not well understood. It is therefore difficult to establish the detailed mechanism, especially in those cases when the transfer is phonon assisted.

For several years we have been interested in the energy levels and energy transfer processes in the cubic hexachloroelpasolites $Cs_2NaLnCl_6$ [2–6]. In these systems the lanthanide ion occupies a perfect octahedral site, surrounded by six chloride ions. The electronic spectra are therefore dominated by magnetic dipole allowed pure electronic origins and electric dipole allowed vibronic origins enabled by Herzberg–Teller coupling. The three odd parity vibrations of the $LnCl_6^{3-}$ ion (ν_3, ν_4 and ν_6) which appear strongly in the vibronic sideband (where allowed by first-order symmetry selection rules), are perturbed by vibrational dispersion and accompanied by weaker lattice vibrations. Progressions in the even parity modes are weak since the potential surfaces of all states derived from a given f^n configuration are closely similar in the nuclear space.

These high-symmetry crystals are attractive model systems for a study of energy transfer processes. First, the transition dipoles associated with the f $\leftrightarrow$ f transitions at octahedral sites are relatively small so that the radiative lifetimes of the excited states are long. Second, the number of excited energy levels is minimized, which reduces the number of possible energy transfer mechanisms. Third, the vibrational dispersion ensures that the vibronic sidebands are much broader than the electronic origins in systems such as LaF_3 so that the sensitivity of the energy transfer to the exact positions of the electronic states will be less and the effects of homo- and heterogeneous broadening should be less important. The energy levels in the lanthanide hexachloroelpasolites are well understood [7]. The Herzberg-Teller vibronic couplings in these systems are also of current interest [3, 8].

An essential prerequisite to understanding the energy transfer between dissimilar ions is to study the cross-relaxation processes and the migration of the excitation in the pure elpasolites and for the $LnCl_6^{3-}$ ions diluted into hosts with no energy levels that can be involved in the transfer process. In this paper we consider the case of migration and relaxation of the $^5D_1$ excited state in $Cs_2NaY_{1-x}Eu_xCl_6$ and $Cs_2NaEuCl_6$.

2. Energy levels, structural and vibrational properties of $Cs_2NaEuCl_6$ and Cs_2NaYCl_6

Both $Cs_2NaEuCl_6$ and Cs_2NaYCl_6 crystallize at room temperature in a face-centred cubic lattice ($Fm3m$) with $a = 10.8095(8)$ and $10.7315(15)$ Å respectively [9]. In common with the $Cs_2NaLnCl_6$ compounds of the larger lanthanides, the europium hexachloroelpasolite undergoes a phase transition at about 90 K which results in two non-equivalent sites probably due to a slight rotation of the $EuCl_6^{3-}$ ions [5]. Whilst this results in spectral splittings of the order of 1 cm^{-1}, this does not result in any observable changes in the $^7F_0 \rightarrow {}^5D_0$ excitation spectrum or the $^5D_0 \rightarrow {}^7F_J$ ($J = 0 \rightarrow 5$) luminescence spectrum. There is no evidence for phase transitions in Cs_2NaYCl_6 or $Cs_2NaY_{1-x}Eu_xCl_6$.

The vibrational properties of $Cs_2NaLnCl_6$ are well understood. The infrared active Eu–Cl stretching ($\nu_3, \tau_{1u}TO$) and bending ($\nu_4, \tau_{1u}TO$) modes of the $EuCl_6^{3-}$ ion have wavenumbers of about 253 and 112 cm^{-1} respectively in $Cs_2NaEuCl_6$ [10]. Lattice modes occur at about 56 and 167 cm^{-1}, the latter being essentially a sodium displacement motion. The IR inactive $\nu_6(\tau_{2u})$ mode occurs at about 80 cm^{-1}, as derived from the luminescence spectra [3]. In the Raman spectra of $Cs_2NaEuCl_6$ the ν_1, ν_2 and ν_5 modes are active at 302, 215 and 121 cm^{-1} respectively, as well as a zone centre lattice mode at about 44 cm^{-1} [11].

The $^5D_1$ state of Eu^{3+} in the hexachloroelpasolite lattice is located 18 963 cm^{-1} above the $^7F_0$ ground state, and 1754 cm^{-1} above $^5D_0$ [3, 5] (figure 1). The next excited state, $^5D_2$ is 2436 cm^{-1} further to high energy. Luminescence from both $^5D_1$ and $^5D_0$ occurs to the ^7F_J ($J = 0 \rightarrow 6$) states and the energy and the vibronic structure of these transitions has been thoroughly investigated [3]. The $^5D_1-{}^5D_0$ energy separation spans about six quanta of the highest energy vibration (302 cm^{-1}) and the non-radiative decay from a $J = 1$ to a $J = 0$ state is formally forbidden [12]. Multiphonon relaxation of $^5D_1$ is therefore inefficient.

3. Experimental details

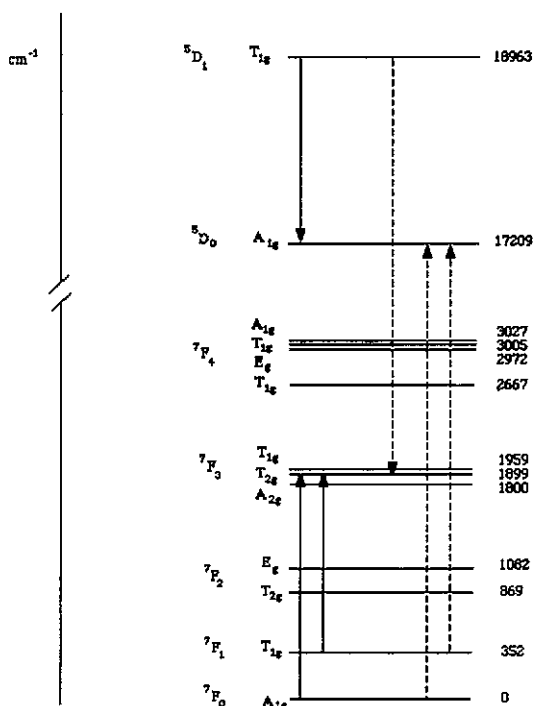Good quality crystals of stoichiometries $Cs_2NaY_{1-x}Eu_xCl_6$ ($x = 0.01, 0.05$ and 0.10)

Figure 1. Energy levels of Eu^{3+} in $Cs_2NaLnCl_6$ up to 19000 cm^{-1}. The cross-relaxation mechanisms (2) and (3) are shown. The processes indicated by full and broken lines are conjugate.

and $Cs_2NaEuCl_6$ were grown at $850\,°C$ in evacuated quartz ampoules by the Bridge-man method [5]. The Eu_2O_3 and Y_2O_3 employed were of 99.99% (Berkshire Ores) quality. Analysis of one of the crystals by inductively coupled plasma atomic emission spectroscopy showed the presence of Nd and Ce at 40 ppm relative to Eu as unity. The crystals were stored over magnesium perchlorate after a careful coating with high vacuum grease in order to reduce their exposure to atmospheric water to a minimum.

Absorption and luminescence spectra were measured as previously described [3, 13]. Decay curves of the luminescence were measured using two dye-laser excitation systems. One (at Kemisk Laboratorium IV, H. C. Ørsted Institutet, Copenhagen) em-ployed a Molectron nitrogen laser pumping a Molectron D100 dye laser, with Coumarin 500 as the laser dye. The sample was maintained in an Air Products Displex system and the luminescence analysed by a 0.5 m monochromator, detected by an EMI 9558 QA photomultiplier, amplified and digitized to 12 bits and averaged over 1000 pulses before transferring the data to a 286-based microcomputer. The second system (at Birkbeck College) consisted of a Spectron Laser dye laser pumped by a frequency doubled Nd:YAG laser (Spectron Laser), with Coumarin 500 as the laser dye. The du-ration of the pulses was less than 10 ns. The samples were maintained under vacuum in a simple laboratory-built liquid nitrogen cryostat. The emission was analysed by a Spex Minimate monochromator and detected by a cooled RCA C31034 A photo-multiplier. The signals were averaged over about 1000 pulses with a modified PAR TDH-9 Waveform Eductor (calibrated and tested following the recommendations of the manufacturer) and transferred to a BBC microcomputer.

The reproducibility of the decay curves was checked by measuring the luminescence from crystals originating from different preparations for each composition. The uncertainties we report for the results extracted from the experimental decay curves is due to both instrumental uncertainties and to the range of results coming from different crystals. For exponential curves the sample variability dominates. After allowing for the different instrumental characteristics of the two systems, the results were entirely consistent. No radiation trapping effects were detected. The experimental decay curves were fitted to various theoretical models using a non-linear least squares simplex procedure.

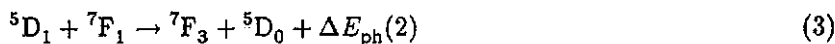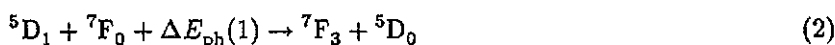## 4. Results and discussion

4.1. $Cs_2NaY_{0.99}Eu_{0.01}Cl_6$

The decay curve of the luminescence from the $^5D_1$ state of Eu^{3+} in our most dilute crystals corresponding to the composition $Cs_2NaY_{0.99}Eu_{0.01}Cl_6$ (excitation wavelength 527.3 nm, in the $^7F_0 \rightarrow {}^5D_1$ transition; observation wavelength 559.0 nm, in the $^5D_1 \rightarrow {}^7F_2(T_{2g})$ transition) is exactly exponential at 80 K over more than 6 halflives with a decay constant $k = (1.36 \pm 0.08) \times 10^2$ s^{-1}. At higher temperatures this decay constant steadily increases and the decay curve becomes non-exponential showing a deviation towards a faster decay for very short times.
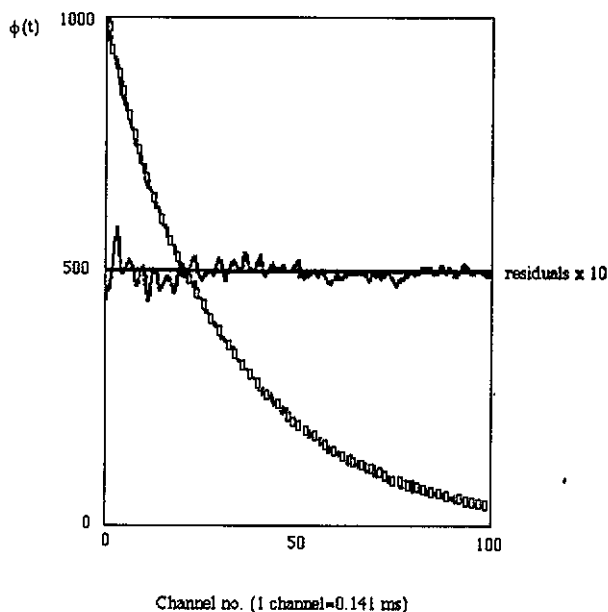
The energy level diagram indicates that no resonant energy transfer is possible from the $^5D_1$ state. This and the temperature dependence suggests that a phonon-assisted process is involved. Energy transfer involving magnetic dipole transitions are expected to be insignificant [14]. At this low concentration of Eu^{3+}, migration of the excitation among the $^5D_1$ donor states is expected to be very slow and many-body processes will be negligible [15]. It is therefore reasonable to attempt to account for the observed kinetics using the Inokuti–Hirayama expression for the decay of the luminescence intensity $\phi(t)$ in the presence of energy transfer due to electric multipolar interactions between the donor and the acceptor [16]:

$$\phi(t) = \phi(0)\exp(-k^0 t - \tfrac{4}{3}\pi\Gamma\left(1 - \frac{3}{s}\right)N_A R_0^3 (kt)^{3/s}). \tag{1}$$

N_A is the concentration of the acceptor ions (ions cm^{-3}), R_0 is a critical donor–acceptor distance, at which the energy transfer rate is identical to the decay rate k^0 of the isolated donor and $s = 6, 8$ or 10 for dipole–dipole (ED–ED), dipole–quadrupole (ED–EQ) or quadrupole–quadrupole (EQ–EQ) interactions respectively. The transfer rate for a donor–acceptor separation R is αR^{-s}. The experimental 293 K decay curve is perfectly fitted using equation (1) with $s = 6$ (ED–ED interactions) (figure 2), whilst the sums of the squares of the residuals are at least 50% greater using $s = 8$ of $s = 10$ and the residuals show a sinusoidal dependence on time. The internal decay rate extracted from the fitting of the 293 K decay curve is $k^0 = (2.0 \pm 0.3) \times 10^2$ s^{-1}.

The two most probable (i.e. having the smallest energy mismatch) phonon-assisted mechanisms for the energy transfer are (figure 1):

$$^5D_1 + {}^7F_0 + \Delta E_{ph}(1) \rightarrow {}^7F_3 + {}^5D_0 \tag{2}$$

$$^5D_1 + {}^7F_1 \rightarrow {}^7F_3 + {}^5D_0 + \Delta E_{ph}(2) \tag{3}$$

$\phi(t)$

residuals x 10

Channel no. (1 channel=0.141 ms)

Figure 2. Decay curve of the luminescence from the $^5D_1$ state of Eu^{3+} in $Cs_2NaY_{0.99}Eu_{0.01}Cl_6$ ($\lambda_{exc} = 527.3$ nm, $\lambda_{obs} = 559.0$ nm) at 293 K, showing the fit to (1). The residuals of the fit are also shown.

where $\Delta E_{ph}(1) = 54, 149$ or 210 cm^{-1} and $\Delta E_{ph}(2) = 152, 211$ or 306 cm^{-1}, depending on which crystal field component of $^7F_3$ is the terminal state.

The excellent fit of the experimental 293 K decay curve using equation (1) with $s = 6$ suggests that the energy transfer occurs due to ED–ED interactions. Since the $EuCl_6^{3-}$ ions are at perfect O_h sites in Cs_2NaYCl_6, this mechanism for the energy transfer requires the coupling of electric dipole vibronic transitions on the Eu^{3+} centres [17]. The phonon-assisted process therefore involves the creation or the annihilation of two ungerade phonons. The energy mismatches $\Delta E_{ph}(1)$ and $\Delta E_{ph}(2)$ can be bridged by several combinations of the internal ungerade modes ν_6, ν_4 and ν_3. The strong temperature dependence of the transfer, which is frozen out already at 80 K, qualitatively agrees with both (2) (through the absorption of two phonons) and (3) (through the involvement of the thermally populated $^7F_1$ state) but does not provide any additional information. As it is not possible to decide which mechanism dominates the transfer, we assign it to a superposition of the cross-relaxations (2) and (3).

The critical distance R_0 for the transfer at 293 K depends on N_A and then on the population of the initial state of the acceptor and ranges from 10 Å for a pure mechanism (2) to 12 Å for a pure mechanism (3). The dipole–dipole coupling parameter α (derived from R_0) ranges from the value 2×10^{-52} m^6 s^{-1} for a pure mechanism (2) to 6×10^{-52} m^6 s^{-1} for a pure mechanism (3). These values can be compared with $\alpha \approx 2 \times 10^{-53}$ m^6 s^{-1} obtained for the non-resonant transfer

$$^2F_{5/2}(Yb^{3+}) + {}^5I_8(Ho^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^5I_6(Ho^{3+}) \tag{4}$$
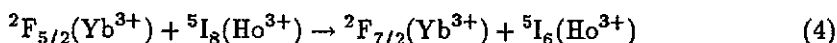
in $Y_{1-x-y}Yb_xHo_yF_3$, with x and y in the range 0.01–0.1, at room temperature [18], for which the energy mismatch is significantly greater (≈ 1500 cm^{-1}) and cannot be bridged by one phonon.

The difference between the decay constant at 80 and 293 K is due mainly to the coth dependence of the vibronic transition dipoles from the $^5D_1$ state to all of the components of the ^7F_J states. Calculation of the weighted average wavenumber of the phonons involved gives results in the region of 250 cm^{-1} which is close to the experimental wavenumber of ν_3. However, the decay constant measured at 80 K is an upper limit of the decay constant in the absence of energy transfer at that temperature since very small deviations from exponential decay cannot be easily identified. If the true internal decay constant of the $^5D_1$ state of EuCl$_6^{3-}$ at 80 K is in the region of 100 s^{-1}, this would correspond to an average weighted phonon wavenumber of about 200 cm^{-1} which is comparable with the value deduced from the vibronic spectrum [3].

4.2. Cs$_2$NaEuCl$_6$

The decay curves of the luminescence from the $^5D_1$ state of the undiluted Cs$_2$NaEuCl$_6$ crystals are exactly exponential for more than six halflives at both 293 and 80 K. The decay rates extracted from the exponential fitting are $(1.52 \pm 0.08) \times 10^4$ s^{-1} at 293 K and $(1.9 \pm 0.1) \times 10^3$ s^{-1} at 80 K. The luminescence from the $^5D_1$ state is therefore strongly quenched by energy transfer processes. The efficiency of the energy transfer η_T [2] is 0.987 at 293 K and 0.928 at 80 K. The exponential shape of the experimental decay curves indicates that for the concentrated crystal the process occurs in the rapid transfer limit [19].

After excitation in the $^5D_1$ state, the emission intensity from the $^5D_0$ state initially rises exponentially with time, and then decays in a strongly non-exponential way at 293 and 80 K [20]. The rise rate constant of the $^5D_0$ emission is identical to the decay rate of the $^5D_1$ state confirming that the $^5D_0$ state is exclusively populated from the $^5D_1$ state.

From the experimental values of the decay rates k (for Cs$_2$NaEuCl$_6$) and k^0 (for the isolated donor), the energy transfer rate $k_{ET} = k - k^0$ can be extracted. k_{ET} is given by [19]

$$k_{ET} = x_A \sum_n W_{0n} \tag{5}$$

where x_A is the probability of the occupation of a site by an acceptor and W_{0n} is the transfer probability from a donor at site 0 to an acceptor at site n. The values of k_{ET} are 1.5×10^4 s^{-1} at 293 K and 1.8×10^3 s^{-1} at 80 K. The temperature dependence of k_{ET} [$k_{ET}(293\text{ K})/k_{ET}(80\text{ K}) \approx 8$] agrees again qualitatively with cross-relaxation (2) (through the temperature dependence of W_{0n}) and with cross-relaxation (3) (through the temperature dependence of x_A). These results are consistent with the energy transfer occurring through a superposition of (2) and (3).

In the case of the rapid transfer, the upper limit for the energy transfer rate is given by the probability of transfer from a donor to a nearest-neighbour acceptor. For a Eu–Eu nearest-neighbour distance of 7.6 Å, using the relation $k_{ET} = \alpha R^{-6}$ and the α values determined for $x = 0.01$ at 293 K, we evaluate a limiting transfer rate in the region 0.6–1.9 $\times 10^4$ s^{-1} which includes the experimental value 1.5×10^4 s^{-1}. The cross-relaxation in the concentrated crystal therefore occurs predominantly from a donor to a nearest-neighbour acceptor.

The experimental data for $x = 1$ in the rapid transfer limit cannot give information about the extent to which resonant migration of the excitation among the donor states is present in this crystal.

4.3. $Cs_2NaY_{0.95}Eu_{0.05}Cl_6$ and $Cs_2NaY_{0.90}Eu_{0.10}Cl_6$

The decay curves at 293 K of the luminescence from $^5D_1$ in $Cs_2NaY_{0.95}Eu_{0.05}Cl_6$ and $Cs_2NaY_{0.90}Eu_{0.10}Cl_6$ are markedly non-exponential but tend to exponential behaviour at long times. The rate constant for the long-time decay is significantly larger than for the isolated donors. Attempts to fit them with the Inokuti–Hirayama model for electric multipolar interactions (equation (1)) and to the Yokota and Tanimoto model [21, 22] for diffusion of the excitation in the case of donor–acceptor dipole–dipole interactions were not successful. This complex behaviour is typical of systems in which the donor–acceptor energy transfer occurs at a rate comparable with the migration rate and has been observed previously for systems such as $La_{1-x}Nd_xF_3$ in the concentration range $0.003 \leq x \leq 0.1$ and in the temperature range 30–300 K [23].

It is extremely unlikely that the migration among the $^5D_1$ excited states involves the resonant coupling of the $^7F_0 \leftrightarrow {}^5D_1$ no-phonon electronic transitions, since they are purely magnetic dipole allowed, and the interactions among magnetic multipoles are negligible [14]. The migration process may therefore involve two mechanisms. First, two $^7F_1 \leftrightarrow {}^5D_1$ transitions on adjacent centres, being formally electric quadrupole allowed and giving rise to an EQ–EQ interaction with a strong temperature dependence. Second, two vibronically allowed $^7F_0 \leftrightarrow {}^5D_1$ transitions on adjacent centres, giving rise to an ED–ED interaction. This requires the creation of an ungerade phonon on one centre and its annihilation on the adjacent centre and will have a weaker temperature dependence. The exchange interaction is not considered due to the large Eu–Eu nearest-neighbour distance ($\approx$ 7.6 Å) in agreement with the conclusions of Blasse *et al* [24] for energy migration among Gd^{3+} ions. The fact that migration is still present at low temperatures (see later) might be cited as evidence in favour of the ED–ED mechanism, with the internal ungerade vibrations, or low-frequency lattice vibrations enabling the vibronic transitions.

In the case of ED–ED interactions for both the donor–acceptor transfer and the donor–donor migration, defined by the coupling parameters α and β, when $\alpha \gg \beta$ a diffusion model has proved to be adequate to describe the transfer processes, whilst for $\alpha \leq \beta$ a hopping model is needed [19]. Both models predict for long times an exponential tail for the decay, characterized by a decay constant $k_t = k^0 + k_M$, where k_M is given by different expressions in the case of diffusion and hopping [25]:

$$k_M(\text{diff.}) = 21N_DN_A\alpha^{1/4}\beta^{3/4} \tag{6}$$

$$k_M(\text{hop.}) = 20N_DN_A\alpha^{1/2}\beta^{1/2} \tag{7}$$

where N_D and N_A are the concentrations of the donors and acceptors, respectively; in the present case they are both Eu^{3+} ions. The fact that migration has a comparable rate to cross-relaxation for relatively low fractional concentrations of Eu^{3+} ($x = 0.05$) indicates that a hopping model is probably adequate for the description of the energy transfer processes in the intermediate concentration range.

The experimental decay curves at 293 K for $Cs_2NaY_{0.95}Eu_{0.05}Cl_6$ and $Cs_2NaY_{0.90}Eu_{0.10}Cl_6$ show a long-time exponential tail yielding values of k_M of $(4.2 \pm 0.4) \times 10^1$ s^{-1} for $x = 0.05$ and $(1.7 \pm 0.2) \times 10^2$ s^{-1} for $x = 0.10$. For these two concentrations the theoretical dependence of k_M upon the product of N_D and N_A is obeyed. Under the assumption that the donor–donor interaction is due to an ED–ED coupling and using the expression of k_M in the case of hopping we obtain values for β in the region $1-2 \times 10^{-52}$ m^6 s^{-1}. These values are consistent with a migration regime approaching the hopping model.

At low temperatures the decay behaviour of $^5D_1$ in $Cs_2NaY_{0.95}Eu_{0.05}Cl_6$ is different from $Cs_2NaY_{0.90}Eu_{0.10}Cl_6$. The 80 K decay curve for $x = 0.05$ is perfectly exponential for more than six halflives, and the decay rate $k = (1.36 \pm 0.08) \times 10^2$ s^{-1} is identical to the value of the internal decay rate k^0 obtained for $Cs_2NaY_{0.99}Eu_{0.01}Cl_6$. This is a clear indication that for $x = 0.05$ at this temperature the energy migration and transfer processes are inefficient and that the decay is only internal. Conversely, the low-temperature decay curves for $x = 0.10$ maintain their non-exponential behaviour, already observed at 293 K, down to the lowest temperatures, and only the 12 K decay curve can be acceptably fitted with an exponential model. The deviation from the exponential decay increases and the overall decay becomes faster as the temperature is increased. The decay behaviour at all temperatures is similar to the one observed at 293 K and characterized by an exponential tail at long times (roughly beyond the time corresponding to a 10-fold decrease in the initial emission intensity).

The decay rates k_t extracted from the exponential fitting of the long-time tail are shown in figure 3 as a function of the temperatures in the 12–320 K range. k_t is almost constant for temperatures up to about 40 K, then the increase is much more pronounced up to about 300 K.
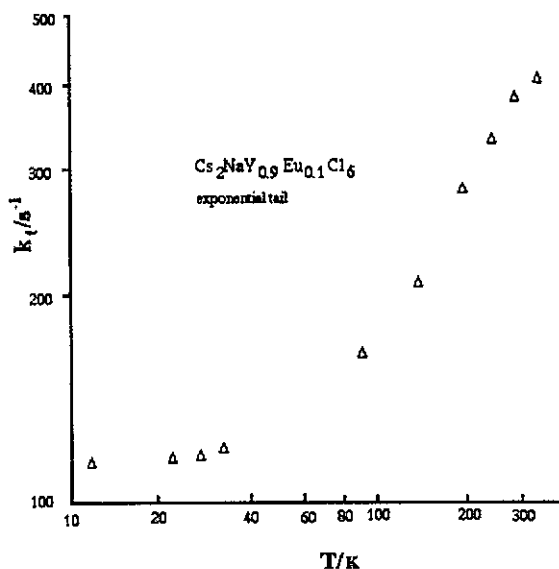

Figure 3. Temperature dependence of the long-time exponential decay rate k_t of the $^5D_1$ state in $Cs_2NaY_{0.90}Eu_{0.10}Cl_6$.

The theoretical explanation of this curve is complex since it contains the temperature dependence of both α and β, and the temperature dependence of the former is unknown. The presence of an exponential tail with decay rate k_t significantly larger than k^0 for $T > 30$ K indicates that the migration of the excitation is active down to low temperatues. At 12 K, the decay curve is virtually exponential with $k = (1.20 \pm 0.10) \times 10^2$ s^{-1}, which approaches the internal decay rate at that temperature, where all migration and transfer processes are frozen.

5. Conclusions

We have shown that energy transfer processes are important determining the kinetics of the luminescence from the $^5D_1$ state in $Cs_2NaY_{1-x}Eu_xCl_6$ ($x = 0.01$–1) at temperatures in the range 293–12 K. Even for the most dilute crystal with $x = 0.01$ at room temperature cross-relaxation processes, occurring through a vibronic electric dipole–electric dipole interaction involving odd parity phonons on the Eu^{3+} centre, are needed in order to account for the experimental decay curves. When the fractional concentration of Eu^{3+} is increased, the cross-relaxation becomes faster, until for the pure crystal the nearest-neighbour donor–acceptor transfer becomes dominant and the emission is strongly quenched. There is evidence for migration of the excitation among the donor states; this process in the intermediate concentration range shows a probability comparable with the cross-relaxation. The high symmetry of the site occupied by the Eu^{3+} ions in these crystals gives rise to a simple energy levels diagram and to well-defined selection rules for the electronic transitions; these two factors have proved to be important in the identification and the characterization of the energy transfer and energy migration processes. The results obtained in the study of this model system can be expected to extend the understanding of the luminescence kinetics of the $^5D_1$ state in other Eu^{3+}-containing materials, especially of technological relevance.

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