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## Energy migration and transfer in the $^5D_0$ state of $Cs_2NaEuCl_6$

Marco Bettinelli† and Colin D Flint‡

† Dipartimento di Chimica Inorganica, Metallorganica ed Analitica,  
Universita' di Padova, Via Loredan 4, 35131 Padova, Italy

‡ Laser Laboratory, Department of Chemistry, Birkbeck College, University of London,  
Gordon House, 29 Gordon Square, London WC1H 0PP, UK

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**Abstract.** Luminescence decay curves from the  $^5D_0$  state of the cubic hexachloroelpasolite crystals  $Cs_2NaEuCl_6$  have been measured over the temperature range 12–340 K. The decay curves are markedly non-exponential, especially at low temperatures and are not well described by standard kinetic treatments. Energy migration in the  $^5D_0$  state occurs at all temperatures studied. Below 75 K an exchange mechanism is important for the migration, whilst at higher temperatures a vibronic electric dipole mechanism dominates. Emission occurs from both the regular and defect sites. The defect sites have a similar energy but a much shorter lifetime than the regular sites, the fast decay being the result of an accompanying fast non-radiative process. Energy migration, energy transfer to defects and relaxation at both defect and regular sites occur at comparable rates which, together with back-transfer from the defect sites, account for the complex kinetics.

### 1. Introduction

For several years we have been interested in the energy levels and energy transfer processes in the cubic hexachloroelpasolites  $Cs_2NaLnCl_6$  [1–6]. In these systems the lanthanide ion occupies a perfect octahedral site, surrounded by six chloride ions and the interlanthanide distances are large and well defined. The electronic spectra are dominated by magnetic-dipole-allowed pure electronic origins and electric-dipole-allowed vibronic origins are enabled by Herzberg–Teller coupling. The three odd-parity vibrations of the  $LnCl_6^{3-}$  ion ( $\nu_3$ ,  $\nu_4$  and  $\nu_6$ ) appear strongly in the vibronic sideband (where allowed by first-order symmetry selection rules) and are 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 migration and transfer processes. Firstly, 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. Secondly, the number of excited energy levels is minimized, which reduces the number of possible energy transfer mechanisms. Thirdly, the vibrational dispersion ensures that the vibronic sidebands are much broader than the electronic origins in the 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 homogeneous 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 [5, 8].

An essential prerequisite to the understanding of the energy transfer between dissimilar ions is to study the cross-relaxation processes and the migration of the excitation in the pure elpasolites. In this paper we consider the case of migration and relaxation of the  $^5D_0$  excited state of  $Cs_2NaEuCl_6$ . We show that the luminescence decay curves following resonant excitation into this state are quite different from those of the  $^5D_1$  state of the same compound [6] because the energy transfer mechanisms are different. The energy migration mechanism is strongly dependent on temperature, both exchange and vibronic electric-dipole–electric-dipole mechanisms being involved.

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

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 because of a slight rotation of the  $EuCl_6^{3-}$  ions [4]. Whilst this results in some spectral splittings of the order of  $1\text{ cm}^{-1}$ , it does not lead to 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, nor does it result in any discontinuities in the variation of the relaxation rates with temperature.

The vibrational properties of  $Cs_2NaLnCl_6$  are well understood and have been summarized in our previous paper [6]. The  $^5D_0$  state of  $Eu^{3+}$  in the hexachloroelpasolite lattice is located  $17\,209\text{ cm}^{-1}$  above the  $^7F_0$  ground state, and the  $^5D_1$  state lies  $1754\text{ cm}^{-1}$  [2, 4] higher in energy (a figure is given in [6]). The next excited state,  $^5D_2$ , is  $2436\text{ cm}^{-1}$  higher in energy. Luminescence from both the  $^5D_1$  and the  $^5D_0$  states occurs to the  $^7F_J$  ( $J = 0 \rightarrow 6$ ) states and the energy and the vibronic structure of these transitions have been thoroughly investigated [2]. The  $^5D_0 \rightarrow ^7F_J$  energy separation spans more than 35 quanta of the highest energy vibrations ( $302\text{ cm}^{-1}$ ); multiphonon relaxation of the  $^5D_0$  state is therefore negligible.

## 3. Experimental details

Good-quality crystals of  $Cs_2NaEuCl_6$  were grown as previously described [6]. Since defect states play an important part in the luminescence decay kinetics, we studied crystals from five different preparations using  $Eu_2O_3$  from three different sources. Analysis of one of the crystals by ICPAES showed the presence of Nd and Ce at 40 ppm relative to Eu as unity, but no other lanthanides were detected above 4 ppm. The numerical results of the energy transfer experiments for each crystal showed a variation that was greater than the experimental error, but we interpret them in a consistent way. We attribute this variation to small differences in the amount of interstitial water in the individual crystals. We therefore present the results for one crystal in detail.

The measurements were carried out using both of the systems described in [6] and the results were compatible. All the quantitative measurements were carried out using

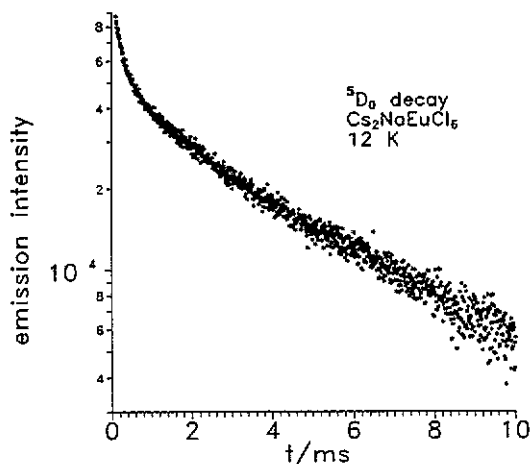


Figure 1. The initial 10 ms (1000 points) of the semilogarithmic plot of the decay curve of the luminescence from the  ${}^5\text{D}_0$  state of  $\text{Cs}_2\text{NaEuCl}_6$  ( $\bar{\nu}_{\text{exc}} = 17\,321\text{ cm}^{-1}$ ,  $\bar{\nu}_{\text{obs}} = 16\,260\text{ cm}^{-1}$ ) at 12 K. The decay curve was measured to 30 ms at increased sensitivity for the extraction of the long-time exponential decay rate.

excitation into the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0 + \nu_4$  vibronic transition and observing the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition. The optical density of the crystals at the excitation wavelength is extremely small and the powers of unfocused laser beams were limited to a few millijoules or less. Biexcitonic effects may therefore be eliminated.

#### 4. Results and discussion

At 12 K the emission from the resonantly excited  ${}^5\text{D}_0$  state of  $\text{Cs}_2\text{NaEuCl}_6$  shows a strongly non-exponential decay (figure 1). The initial decay corresponds to a rate constant  $k$  in the region of  $3500\text{ s}^{-1}$  whilst the long-time limit of the decay gives a rate constant of  $k = 180 \pm 20\text{ s}^{-1}$ . This 'exponential tail' does not approach the low-temperature limit of the decay constant of the  ${}^5\text{D}_0$  state of  $\text{Cs}_2\text{NaY}_{0.99}\text{Eu}_{0.01}\text{Cl}_6$  ( $\sim 90\text{ s}^{-1}$ ) where the  $\text{EuCl}_6^{3-}$  ions are effectively isolated from each other. Clearly a process that is not present in the dilute materials is quenching the emission in  $\text{Cs}_2\text{NaEuCl}_6$ . The lowest order many-body process would involve the coupling of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_6$  transition on one site to at least three other  ${}^7\text{F}_0 \rightarrow {}^7\text{F}_6$  transitions on neighbouring ions and so may easily be eliminated. It is therefore necessary to invoke quenching by an impurity. During the measurement of the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  excitation spectra of the crystals at low temperatures [4] we observed the presence of a second type of europium centre with a much shorter luminescence lifetime and that gave a broader luminescence spectrum generally similar to that of the majority species. Only one feature of the excitation spectrum of this species was identified, some  $41\text{ cm}^{-1}$  higher in energy than the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition of the majority species.

The most probable impurity in the  $\text{Cs}_2\text{NaEuCl}_6$  crystals is water; we have previously noted that the crystals are very hygroscopic and that the absorption of water reduces the luminescence lifetime [2]. Indeed it is clear from the reported lifetimes in that paper that the crystals had been affected by moisture uptake. The presence of water was detected during the measurement of the  ${}^7\text{F}_0 \rightarrow {}^7\text{F}_1$  transitions in the infrared spectral region [10]. It is plausible therefore that all of our crystals contain a small quantity of interstitial water and that the broadened spectrum is from a  $\text{EuCl}_6^{3-}$  ion with a neighbouring water molecule. Water molecules are known to relax excited states efficiently [11], four

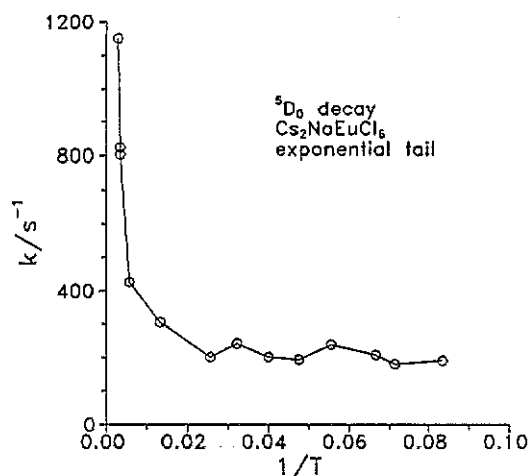


Figure 2. Temperature dependence of the long-time exponential decay rate  $k$  of the  ${}^5D_0$  state in  $\text{Cs}_2\text{NaEuCl}_6$ .

quanta of a hydrogen-bonded O—H vibration would span the energy gap to the ground manifold. We note that, whilst the decay constant measurements for the crystals discussed in [2] show that they contained far more water than any of the crystals used in the current study, the  ${}^5D_0$ – ${}^7F_j$  spectra were very similar to those obtained here. Thus the decay constants are much more sensitive to the presence of moisture than the appearance (excluding the absolute intensities) of the luminescence spectrum.

As the temperature is raised, the initial rate increases only slowly, becoming about  $4000\text{ s}^{-1}$  at  $340\text{ K}$  whilst the rate constant for the exponential tail stays approximately constant up to  $39\text{ K}$  and then increases rapidly reaching  $1150\text{ s}^{-1}$  at  $340\text{ K}$  (figure 2). At the highest temperatures the curves are still clearly non-exponential but less so than at low temperatures.

As a first step in the analysis of these curves we attempted to fit the decay curves to the Inokuti–Hirayama expression for the decay of the luminescence intensity  $\varphi(t)$  in the presence of energy transfer resulting from electric multipolar interactions between the donor and the acceptor in the absence of migration amongst the donors [12]:

$$\varphi(t) = \varphi(0) \exp[-k^0 t - \frac{3}{8}\pi\Gamma(1 - 3s^{-1})N_A R_0^3 (k^0 t)^{3/s}]. \quad (1)$$

$N_A$  is the concentration of the acceptor ions (ions/cm<sup>3</sup>),  $R_0$  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  $\alpha R^{-s}$ , where  $\alpha$  is the interaction between the donors  $D$  and the acceptors  $A$ . Whilst this expression reproduces the overall shape of the curve, the fits are unconvincing regardless of the value of  $s$  chosen. The residuals are large and have a sinusoidal dependence on time.

A property of this model is that for sufficiently long times all of the donors with acceptors within range are relaxed so that the decay becomes exponential with time and with a decay constant equal to that of the isolated ion. The time after which the decay curve becomes approximately exponential depends on the ratio of the acceptor concentration  $N_A$  to that of the critical concentration  $N_0$  where  $N_0 = 3/(4\pi R_0^3)$ . For  $N_A/N_0$  ratios in the region of  $0.1$  the initial non-exponential part of the curve is short whilst, for  $N_A/N_0$  ratios in the region of  $1.0$ , the decay curve approaches exponential

behaviour with a decay constant equal to that of the isolated donor after a time of about  $(k^0)^{-1}$  when the intensity has fallen to less than 10% of its initial value [13]. We have therefore fitted the last 10% of decay curve at each temperature to a simple exponential curve. In each case the fit is satisfactory with well distributed residuals; the decay constant extracted is almost constant at 180–200  $\text{s}^{-1}$  up to about 35 K but then increases rapidly to over 800  $\text{s}^{-1}$  at 293 K. These values are so much larger than the decay constant of the isolated ion as to rule out the simple Inokuti–Hirayama model.

In concentrated materials it is common for energy migration amongst the donors to occur. The simple Inokuti–Hirayama model is no longer applicable and the decay kinetics become complex. For a dipole–dipole donor–acceptor interaction and energy migration described by a diffusion model the equation takes the form [14];

$$\varphi(t) = \varphi(0) \exp\{-k^0 t - (N_A/N_0)\Gamma(\frac{1}{2})(k^0 t)^{1/2}[(1 + 10.87y + 15.5y^2)/(1 + 8.743y)]^{3/4}\} \quad (2)$$

where  $y = D(k^0)^{-1}R_0^{-2}(k^0 t)^{2/3}$ ,  $D = \frac{1}{2}(4\pi/3)^{4/3}N_D^{4/3}\beta$  is the diffusion constant and  $\beta$  is the dipole–dipole interaction between the regular Eu donor sites [13]. At short times this expression approaches the Inokuti–Hirayama model but now for long times the migration becomes important so that the decay becomes exponential with a decay constant [13]

$$k = k^0 + k_M$$

where  $k_M = 4\pi DN_D R_s$ , with  $R_s = 0.676(\alpha/D)^{1/4}$ . Clearly for sufficiently large  $\alpha$  and  $\beta$  this can provide an explanation of the values of the rate constants for the exponential tail. The strong temperature dependence of  $k_M$  then reflects the temperature dependence of  $\alpha$  and/or  $\beta$  with the latter likely to dominate. Attempts to fit the whole curve using expression (2) were, however, only slightly more successful than those using (1). We return to this problem later.

Since the decay constants for the exponential tail clearly show the effects of migration it is necessary to consider the possible mechanisms for such a process. The  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  zero-phonon transition at cubic sites is very highly forbidden and has not been unambiguously identified in the excitation and luminescence spectra of  $\text{Cs}_2\text{NaEuCl}_6$  at any temperature. Some crystals do show a weak feature at the expected position [4] but the variable nature of its intensity suggests that it is the result of a transition at a non-cubic defect site. At very low temperatures spectral overlap between the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  donor transition and the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  acceptor transition, both at the regular cubic sites, is therefore vanishingly small. Energy migration by electric or magnetic multipole interactions is then highly unlikely. It is probable therefore that the migration proceeds by an exchange mechanism (in which we include superexchange) and that this mechanism is responsible for  $k_M$  values in the region of 90  $\text{s}^{-1}$ , the difference between the low-temperature decay constant for the exponential tail of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  emission of  $\text{Cs}_2\text{NaEuCl}_6$  and the corresponding exponential decay constant for the isolated  $\text{EuCl}_2^{2-}$  ions. The low value of this migration rate is consistent with the large distance between the  $\text{Eu}^{3+}$  centres.

As the temperature is raised spectral overlap between the vibronic structure of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  donor transition and the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  acceptor transition [4] occurs and energy migration by the electric-dipole–electric-dipole mechanism becomes important because of a rapid increase in the coupling constant  $\beta$ . It would be expected that this will start to occur at temperatures when the zone boundary acoustic phonons and the transverse

optical ( $\tau_0$ ) lattice vibrations are significantly populated but become much more important at temperatures when the infrared-active Cl—Eu—Cl bending ( $\nu_4$ ,  $\tau_{1u}$  TO,  $\bar{\nu} = 112 \text{ cm}^{-1}$ ) mode of the  $\text{EuCl}_6^{3-}$  ion, which dominates the vibronic excitation spectrum of the ion [4], becomes populated. We note that these wavenumbers agree nicely with the slow increase in  $k_M$  values above 35 K and the much more rapid increase above 75 K.

The energy transfer rate to the defect sites does not show a similar strong temperature dependence. It is likely to involve an electric dipole transition at a non-cubic defect overlapping with an electric dipole vibronic transition at the regular sites.

There remains the failure of equation (2) to account for the observed kinetics. This is not unexpected and at least three factors are involved. Firstly the equation is derived on the assumption of no back-transfer from the defect sites to the regular sites. Since the difference in the  $^5\text{D}_0$  energy levels between the regular and defect sites is unlikely to be more than  $10 \text{ cm}^{-1}$  and the regular sites are in enormous excess this is not a reasonable assumption. (The feature observed in the excitation spectrum of the defect is unlikely to be the electronic origin; variable intensity bands coincident with the expected position of the electronic origin of the regular sites are also observed [4].) Secondly, there will be more than one type of defect site. Thirdly, there are a number of approximations in the derivation of equation (2) for this system; we are currently investigating the removal of some of these approximations.

## 5. Conclusions

We have shown that energy migration and energy transfer to defects are important factors in determining the kinetics of the luminescence from the  $^5\text{D}_0$  state in  $\text{Cs}_2\text{NaEuCl}_6$  at temperatures in the range 340–12 K. At temperatures above 75 K energy migration amongst the regular sites is fast, taking place by a vibronic electric dipole process resulting from the overlap of vibronic hot bands (principally that arising from  $\nu_4$ ) in the emission spectra with the corresponding transition in the absorption spectrum and vice versa. The excitation migrates until it encounters a defect Eu site associated (probably) with an interstitial water molecule. Such sites have short lifetimes and the decay of the excitation at these sites, principally by a non-radiative mechanism but with a detectable radiative component, competes efficiently with back-transfer to the regular sites. At lower temperatures the vibronic energy migration is frozen out because of the decrease in intensity of the vibronic hot bands, but migration still occurs, although at a much reduced rate, by an exchange mechanism (which also plays a minor role at higher temperatures). The relaxation of the excitation at the defect sites continues to be fast down to at least 12 K. The kinetics of the decay curves are not well described by the standard model with diffusion resulting, in part, from back-transfer from the defect sites to the regular sites even at low temperatures.

It is of interest to compare this system with that of the  $^5\text{D}_4 \rightarrow ^7\text{F}_7$  emission of  $\text{Cs}_2\text{NaTbCl}_6$ . In this case there is little difference between the decay curves of the pure material and that of  $\text{Cs}_2\text{NaY}_{0.99}\text{Tb}_{0.01}\text{Cl}_6$  at room temperature or liquid nitrogen temperature [5]. One factor that may be important is the larger energy difference between the  $^5\text{D}_4$  and  $^7\text{F}_7$  states. Five quanta of an O—H stretching vibration are now required to span the gap and it is commonly observed that high-frequency oscillators are much less effective in quenching the  $^5\text{D}_4 \rightarrow ^7\text{F}_7$  emission of  $\text{Tb}^{3+}$  than the  $^5\text{D}_0 \rightarrow ^7\text{F}_7$  emission of  $\text{Eu}^{3+}$  [11]. If both the emission spectra and the lifetime of any water-induced defects is comparable with that of the regular sites, the decay curves will be exponential

with a decay constant equal to that of the isolated ion whether energy migration and transport are present or not.

The relaxation processes for the  $^5\text{D}_1$  state of  $\text{Cs}_2\text{NaEuCl}_6$  [6] are quite different from those of the  $^5\text{D}_0$  state in the same material reported in this work. In the  $^5\text{D}_1$  state a very efficient phonon-assisted cross relaxation occurs at 80 K and above since the energy separation of the  $^5\text{D}_1$  and  $^5\text{D}_0$  states is similar to the separation of the  $^7\text{F}_3$  and the  $^7\text{F}_0$ ,  $^7\text{F}_1$  states. This cross relaxation is so fast that transfer to nearest neighbours dominates the relaxation process and exponential decay occurs. From those data it is impossible to determine whether energy migration occurs before this fast cross relaxation, although there is evidence for energy migration in the diluted materials  $\text{Cs}_2\text{NaY}_{1-x}\text{Eu}_x\text{Cl}_6$  ( $x = 0.05, 0.10$ ) where the rate of the cross relaxation is greatly reduced. In the  $^5\text{D}_0$  state of  $\text{Cs}_2\text{NaEuCl}_6$  no cross relaxation can occur since there is no suitable set of acceptor levels. Non-radiative relaxation at a single  $\text{EuCl}_6^{3-}$  ion is inefficient because of the large number of quanta required to span the  $^5\text{D}_0$ - $^7\text{F}_j$  energy separation. Radiative relaxation at a single  $\text{EuCl}_6^{3-}$  ion is slow because of the low transition probability at the centrosymmetric site. Energy migration by both exchange and vibronic electric-dipole-electric-dipole mechanisms, although slow, can therefore compete effectively with all other relaxation processes at the majority sites. This migration usually proceeds until relaxation (predominantly non-radiative) occurs at a defect site.

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