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# TEMPERATURE DEPENDENCE OF LUMINESCENCE DECAY FROM THE $^4G_{5/2}$ STATE OF $Sm^{3+}$ IN $Cs_2NaSm_xY_{1-x}Cl_6$ AND $Cs_2NaSm_xEu_yY_{1-x-y}Cl_6$

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Luminescence decay curves for the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ emission of $Sm^{3+}$ in the cubic hexachloroelpasolite crystals $Cs_2NaSm_xY_{1-x}Cl_6$ ($x = 0.005$ to $x = 1$) and $Cs_2NaSm_xEu_yY_{1-x-y}Cl_6$ ($x = 0.01$ to $x = 0.95$, $y = 0.05$ to $y = 0.99$) have been measured over the temperature range 10 K to 300 K using pulsed laser excitation into the $^4G_{5/2}$ state of $Sm^{3+}$. The luminescence from this state is strongly quenched by cross relaxation to $Sm^{3+}$ acceptors and energy transfer to the $^5D_0$ state of $Eu^{3+}$. The temperature dependence of cross relaxation and of energy transfer is discussed in terms of the involved mechanisms.

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## 1. Introduction

In a series of papers [1–4] a recently developed shell model has been applied to understand the luminescence decay curves for the emission from the $^4G_{5/2}$ state of $Sm^{3+}$ in $Cs_2NaSm_xY_{1-x}Cl_6$ ($x = 0.005$ to $x = 1$) and $Cs_2NaSm_xEu_yY_{1-x-y}Cl_6$ ($x = 0.01$ to $x = 0.95$, $y = 0.05$ to $y = 0.99$).

In the latter material the emission from the $^4G_{5/2}$ state of $Sm^{3+}$ is strongly quenched by both, cross relaxation to nearest neighbour $Sm^{3+}$ ions and energy transfer to the $^5D_0$ state of $Eu^{3+}$. In this contribution attention is focused on the crystals $Cs_2NaSm_{0.01}Eu_yY_{0.99-y}Cl_6$ ($y = 0.05$ to $y = 0.99$) over the temperature range 10 K to 300 K.

According to the shell model for energy transfer the cross-relaxation rate $k^{CR}$ to a single acceptor in the first shell is determined from the measured exponential decay constants for $Cs_2NaSmCl_6$ which is 11600 $s^{-1}$ at 10 K corresponding

$k^{\mathrm{CR}} = 850\ \mathrm{s}^{-1}$ for three-shell dipole–dipole interaction increasing by a factor of 2.7 at 300 K [1].

The energy-transfer rate is determined from results obtained on $\mathrm{Cs_2NaSm_{0.01}Eu_{0.99}Cl_6}$ as $k^{\mathrm{ET}} = 5.5\ \mathrm{s}^{-1}$ at 10 K increasing to $49.9\ \mathrm{s}^{-1}$ at 300 K. The stronger temperature dependence of $k^{\mathrm{ET}}$ indicates that two different mechanisms for energy transfer are involved. The temperature dependencies of $k^{\mathrm{CR}}$ and $k^{\mathrm{ET}}$ are discussed in terms of resonant and phonon-assisted energy transfer.

## 2. The shell model for simultaneous cross relaxation and energy transfer

Within our shell model luminescence decay curves following a $\delta$-function excitation pulse take the form [4]

$$I(t) = I(0)\exp(-k_0 t)$$

$$\times \prod_{n=1}^{\mathrm{shells}} \sum_{r_n=0}^{N_n} \sum_{q_n=0}^{N_n-r_n} O^{N_n}_{N_n,q_n}(x,y)\exp\left[-G^s_n(r_n k^{\mathrm{CR}} + q_n k^{\mathrm{ET}})\left(\frac{R_1}{R_n}\right)^s t\right], \quad (1)$$

where $k_0$ is the intrinsic decay rate of the isolated donor ion including radiative and non-radiative relaxation processes, $k^{\mathrm{CR}}$ is the cross-relaxation rate from the donor ion to a chemically identical acceptor ion in the first shell, and $k^{\mathrm{ET}}$ is the rate of energy transfer to a $n = 1$ acceptor chemically different from the donor. $R_n$ is the distance between the donor and an acceptor in the $n$-th shell. The distance dependence of $k^{\mathrm{CR}}$ and $k^{\mathrm{ET}}$ is included in the value of $s = 6$, 8, or 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. In the elpasolite system contributions with $s > 6$ are not excluded a priori but may be neglected in the following investigation. The occupancy factor $O^{N_n}_{r_n,q_n}(x,y)$ is the probability of finding $r_n$ acceptor ions chemically identical to the donor and $q_n$ chemically different acceptors in the $n$-th shell which has a capacity to contain $N_n$ acceptors [4]. $G^s_n$ is a geometric factor containing the angular dependence of cross-relaxation and energy-transfer processes which is independent of the shell number $n$ for $s = 6$ [5] and will therefore be included in the definitions of $k^{\mathrm{CR}}$ and $k^{\mathrm{ET}}$. As discussed in a previous paper [4] the expansion in Eq. (1) may be truncated at $n = 3$ for the elpasolite lattice.

In our shell model we assume Förster–Dexter multipole–multipole interaction [6, 7] between statistically distributed donor and acceptor ions where the rate of resonant energy transfer from a donor $D$ to an acceptor $A$ may be written

$$k^{\mathrm{ET}} = \frac{2\pi}{\hbar^2}\sum_{d,d'}\sum_{a,a'} p_{d'}p_a |\langle d'a|\hat{H}_{DA}|da'\rangle|^2 \int g_{d'd}(E)g_{aa'}(E)\mathrm{d}E, \quad (2)$$

where $p_{d'} = g_{d'}\exp(-E_{d'}/k_{\mathrm{B}}T)\left[\sum_{d''} g_{d''}exp(-E_{d''}/k_{\mathrm{B}}T)\right]^{-1}$ is the thermal population of the $d'$-th initial donor state with similar notation for the acceptor.

Taking Lorentzian lineshape functions of half widths $\Delta E_{d'd}$ and $\Delta E_{aa'}$ centred at energies $E_{d'd}$ and $E_{aa'}$ the overlap integral in Eq. (2) gives [8]

$$\int g_{d'd}(E)g_{aa'}(E)\mathrm{d}E = \frac{\hbar}{\pi}\frac{\Delta E_{d'd} + \Delta E_{aa'}}{(\Delta E_{d'd} + \Delta E_{aa'})^2 + (E_{d'd} - E_{aa'})^2}. \quad (3)$$

## 3. Results and discussion

The growth of single crystals of high optical quality and the measurements of luminescence decay curves have been described in detail previously [1]. The spectroscopic and vibrational properties of $Cs_2NaSmCl_6$ and $Cs_2NaEuCl_6$ have been investigated both, experimentally and theoretically [9–15]. The electronic spectra are dominated by magnetic dipole allowed electronic origins and electric dipole allowed vibronic origins.

In the $Cs_2NaSm_xEu_yEu_yY_{1-x-y}Cl_6$ crystals a variety of cross-relaxation and energy-transfer pathways exist involving the ${}^6F_J$ ($J$ = 5/2, 7/2, 9/2, 11/2) intermediate states of $Sm^{3+}$ and the ${}^7F_1$ and ${}^5D_0$ states of $Eu^{3+}$ and are shown as in Fig. 1 in Ref. [4].

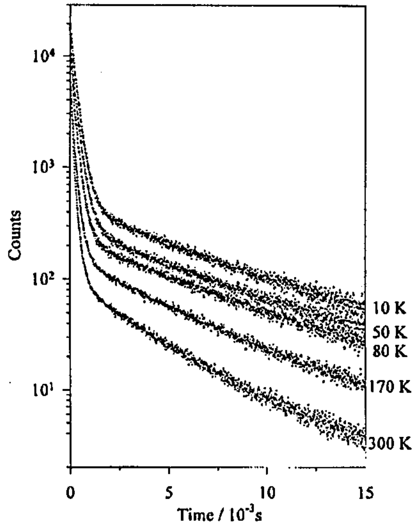

Fig. 1. Time evolution of the ${}^4G_{5/2}$ emission of $Cs_2NaSm_{0.25}Y_{0.75}Cl_6$ as a function of temperature.

Figure 1 shows the temperature dependence of luminescence decay from the ${}^4G_{5/2}$ state of $Sm^{3+}$ in $Cs_2NaSm_{0.25}Y_{0.75}Cl_6$. At all temperatures the decay curves consist of an initial non-exponential fast process followed by a slightly non-exponential slower region. The proportion of the fast process increases with increasing temperature. There is no evidence for a change in the mechanism occurring in this compound over the whole temperature and concentration ranges studied. This would appear to exclude energy migration among the ${}^4G_{5/2}$ state of $Sm^{3+}$ as a significant contributor to the decay kinetics.

The variation of the intrinsic decay rate $k_0$, cross-relaxation rate $k^{\mathrm{CR}}$, and energy-transfer rate $k^{\mathrm{ET}}$ with temperature are shown in Table. A comparison with emission spectra in the ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$, ${}^6H_{7/2}$, and ${}^6H_{9/2}$ regions at 10 K and 300 K [10] shows that the temperature dependence of $k_0$ is entirely consistent with the relaxation mechanism being due to the sum of magnetic dipole transitions

TABLE

Kinetic data for the relaxation of the ${}^4G_{5/2}$ state of $Sm^{3+}$ in $Cs_2NaSm_xEu_yY_{1-x-y}Cl_6$ as a function of temperature (DD indicates that dipole–dipole interaction has been assumed for both cross-relaxation and energy-transfer processes).

| $T$ [K] | $k_0$ [$s^{-1}$] | $k^{CR}$(DD) [$s^{-1}$] | $k^{ET}$(DD) [$s^{-1}$] |
|---|---|---|---|
| 10 | 58.4 | 832 | 5.5 |
| 20 | 58.5 | 870 | |
| 30 | | | 5.7 |
| 40 | 61.8 | 105 0 | |
| 60 | 65.2 | 1160 | |
| 80 | 66.3 | 1270 | 7.2 |
| 100 | 70.3 | 1370 | 8.2 |
| 140 | 77.9 | 1590 | 10.0 |
| 170 | 84.1 | 1700 | 13.0 |
| 200 | | | 15.3 |
| 240 | | | 30.0 |
| 300 | 109 | 2120 | 49.9 |

and electric dipole vibronic transitions. Below 100 K the dependence of $k_0$ on temperature is well described using the coth law [16,17]

$$k_0(T) = k_0(0) \sum_i p_i \coth\left(\frac{h\nu_i}{k_B T}\right) \tag{4}$$

with the sum running over all enabling modes of the lattice with the amount of contribution determined by $p_i$. As the temperature is increased, additional radiative and non-radiative processes involving the thermally populated $({}^4G_{5/2})\ \Gamma_7$ level contribute to the intrinsic decay rate.

The temperature dependence of the cross-relaxation rate between $Sm^{3+}$ ions is slightly stronger but again entirely consistent with an electric dipole vibronic–electric dipole vibronic (EDV–EDV) cross-relaxation mechanism. The stronger temperature dependence of $k^{CR}$ is due to this quantity being proportional to the product of two vibronic mechanisms involving $\nu_6$ and $\nu_4$ as well as $\nu_3$ and the minimum contribution of magnetic dipole processes.

The most probable phonon-assisted mechanisms for cross relaxation having the smallest energy mismatch are

$$({}^4G_{5/2})\Gamma_8 + ({}^6H_{5/2})\Gamma_7 \rightarrow ({}^6F_{11/2})a\Gamma_8 + ({}^6F_{5/2})\Gamma_8, \tag{5a}$$

$$({}^4G_{5/2})\Gamma_8 + ({}^6H_{5/2})\Gamma_7 + \Delta\nu_1 \rightarrow ({}^6F_{11/2})\Gamma_6 + ({}^6F_{5/2})\Gamma_7, \tag{5b}$$

$$({}^4G_{5/2})\Gamma_8 + ({}^6H_{5/2})\Gamma_7 + \Delta\nu_2 \rightarrow ({}^6F_{5/2})\Gamma_7 + ({}^6F_{11/2})a\Gamma_8, \tag{5c}$$

$$({}^4G_{5/2})\Gamma_8 + ({}^6H_{5/2})\Gamma_7 \rightarrow ({}^6F_{5/2})\Gamma_8 + ({}^6F_{11/2})a\Gamma_8, \tag{5d}$$

where $\Delta\nu_1 = 71\ \mathrm{cm}^{-1}$ corresponding to the $\nu_6$ normal mode of the $[\mathrm{SmCl_6}]^{3-}$ entity, and $\Delta\nu_2 = 32\ \mathrm{cm}^{-1}$ which may be bridged by the creation of a lattice phonon mode.

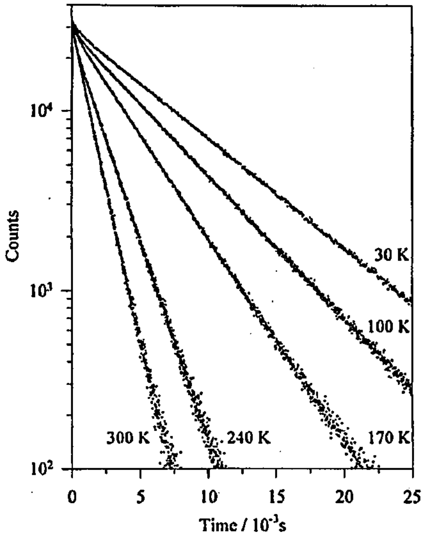

Fig. 2. Temperature dependence of luminescence decay from the ${}^4G_{5/2}$ state of $\mathrm{Sm}^{3+}$ in $\mathrm{Cs_2NaSm_{0.01}Eu_{0.99}Cl_6}$.

The temperature dependence of luminescence decay curves from the ${}^4G_{5/2}$ state of $\mathrm{Sm}^{3+}$ in $\mathrm{Cs_2NaSm_{0.01}Eu_{0.99}Cl_6}$ is shown in Fig. 2. Note that the main contribution to the temperature dependence is due to the energy transfer from $\mathrm{Sm}^{3+}$ donor ions to $\mathrm{Eu}^{3+}$ acceptors. The temperature dependence of the energy-transfer rate indicates that two different mechanisms are involved. At low temperature the most probable mechanism for energy transfer from $\mathrm{Sm}^{3+}$ donor ions to $\mathrm{Eu}^{3+}$ acceptors in the crystals $\mathrm{Cs_2NaSm_xEu_yY_{1-x-y}Cl_6}$ involves the EDV transitions

$$\mathrm{Sm}^{3+} : ({}^4G_{5/2})\Gamma_8 + \mathrm{Eu}^{3+} : ({}^7F_0)\Gamma_1 \rightarrow \mathrm{Sm}^{3+} : ({}^6H_{5/2})\Gamma_8 + \mathrm{Eu}^{3+} : ({}^5D_0)\Gamma_1 + \Delta\nu_{\mathrm{vib}}, \tag{6}$$

where the energy mismatch $\Delta\nu_{\mathrm{vib}} = 395\ \mathrm{cm}^{-1}$ can be bridged by coupling to the odd parity vibrational modes of the $[\mathrm{LnCl_6}]^{3-}$ ions. This energy-transfer mechanism becomes more efficient as the temperature is increased due to the phonon density increasing with $[\exp(h\nu/k_\mathrm{B}T) - 1]^{-1}$, where $h\nu$ is the phonon energy.

At temperatures above 80 K a resonant pathway becomes important,

$$\mathrm{Sm}^{3+} : ({}^4G_{5/2})\Gamma_7 + \mathrm{Eu}^{3+} : ({}^7F_1)\Gamma_4 \rightarrow \mathrm{Sm}^{3+} : ({}^6H_{7/2})\Gamma_7, \Gamma_8 + \mathrm{Eu}^{3+} : ({}^5D_0)\Gamma_1, \tag{7}$$

where both transitions are of magnetic dipole allowed electronic origin.

The temperature dependence of this resonant pathway is introduced by the Boltzmann factors and the normalized lineshape functions of Eq. (2) which depend on the position and width of the donor emission and acceptor absorption lines. A major contribution to homogeneous linebroadening arises from two-phonon Raman scattering processes showing a $T^7$ dependence [18],

$$\Delta E_{d'd} = \alpha \left(\frac{T}{T_D}\right) \int_0^{T_D} \frac{x^6}{\exp(x) - 1} \mathrm{d}x, \tag{8}$$

where $\alpha$ is the electron–phonon coupling parameter, $x = h\nu/k_B T$, and $T_D$ is the Debye temperature of the crystalline lattice.

The energy gaps between the $\Gamma_8$ and $\Gamma_7$ crystal-field levels of the ${}^4G_{5/2}$ state of $Sm^{3+}$ as well as between the ${}^7F_0$ and ${}^7F_1$ states of $Eu^{3+}$ are about 350 $cm^{-1}$. The thermal population of these states becomes 0.1% for $Sm^{3+}$ and 0.5% for $Eu^{3+}$ at 80 K increasing to 9% for $Sm^{3+}$ and 36% for $Eu^{3+}$ at 300 K.

## 4. Conclusions

The temperature dependence of luminescence decay from the ${}^4G_{5/2}$ state of $Sm^{3+}$ in $Cs_2NaSm_xY_{1-x}Cl_6$ ($x = 0.005$ to $x = 1$) and $Cs_2NaSm_{0.01}Eu_yY_{0.99-y}Cl_6$ ($y = 0.05$ to $y = 0.99$) gives no evidence for energy migration among $Sm^{3+}$ donor ions with a rate comparable to the cross-relaxation and energy-transfer rates. The assumption of the cross-relaxation processes occurring by EDV–EDV interaction is manifested by the observed temperature dependence of $k^{CR}$.

For energy transfer from $Sm^{3+}$ donor ions to the ${}^5D_0$ state of $Eu^{3+}$ acceptors two mechanisms are involved. At low temperatures phonon-assisted energy transfer is dominant while resonant transfer involving the magnetic dipole allowed ${}^7F_1 \rightarrow {}^5D_0$ transition of $Eu^{3+}$ becomes important as the temperature is increased.

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