Energy Transfer in some Luminescent Gadolinium Fluorides*

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Gd^{3+} is of great interest as a sensitizer as well as an activator or intermediate ion in host matrices in attempts to achieve lamp phosphors. Energy transfer plays an important role in the efficiency of such phosphors. In a previous paper [1] we reported some results about Gd^{3+} ion behaviour in the two phases α- and β-$RbGd_3F_{10}$. Our purpose in this paper is to compare these results with those obtained in two other fluoride compounds: the concentrated phases $NaGdF_4$ and K_2GdF_5. The energy transfer from Gd^{3+} to Eu^{2+} in cubic $RbGd_3F_{10}$ is also reported.

Results and Discussion

NaGdF₄

$NaGdF_4$ is isostructural with the low temperature form of $NaNdF_4$ [2] (Fig. 1). Gd^{3+} ions are located in two kinds of crystallographic sites with the same C_{3h} symmetry. Each Gd^{3+} ion has two first neighbour fluorides and six second neighbours; one of the sites is fully occupied, the other one is only half occupied.

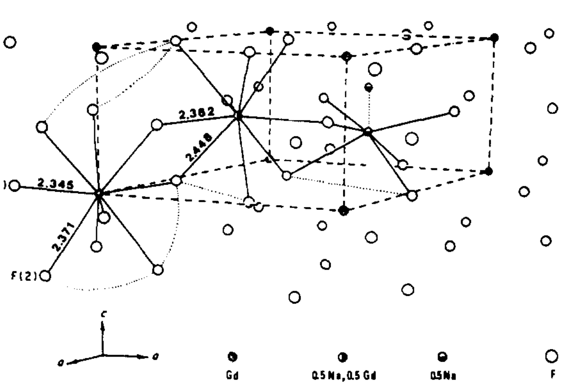

Fig. 1. Schematic crystal structure of $NaGdF_4$.

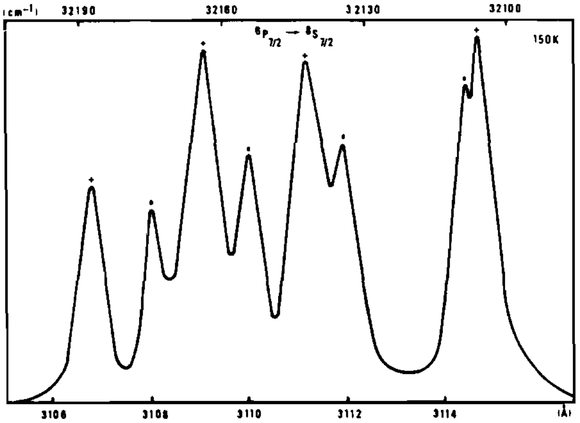

Fig. 2. Emission spectrum of UV fluorescence of $NaGdF_4$ at 150 K.

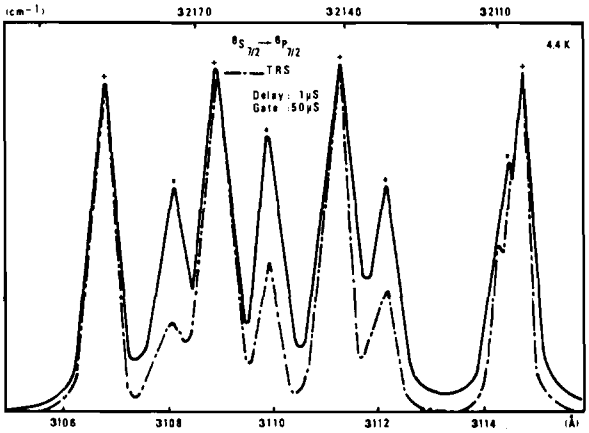

Fig. 3. Excitation spectrum of UV fluorescence of $NaGdF_4$ at 4.4 K.

At a sufficiently low temperature, *i.e.* 150 K, the fluorescence emission spectrum (Fig. 2) of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition displays eight distinct lines. Comparison with a time-resolved excitation spectrum recorded at 4.4 K (Fig. 3) allows one to separate these lines into two groups (0) and (+). The intensity ratio between these two series in Fig. 2 reflects roughly the site occupancy. Moreover, from the spectrum recorded at a short time it can be seen that an energy transfer occurs from one site to the other.

The emission spectrum of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ fluorescence at 4.4 K (Fig. 4) shows besides the intrinsic line (corresponding to the lowest Stark component of the $^6P_{7/2}$ multiplet) as many as six lines attributed to traps. A time-resolved spectrum plotted on the same Figure shows clearly the occurrence of an energy transfer from Gd^{3+} ions in normal sites to Gd^{3+} ions in perturbed sites.

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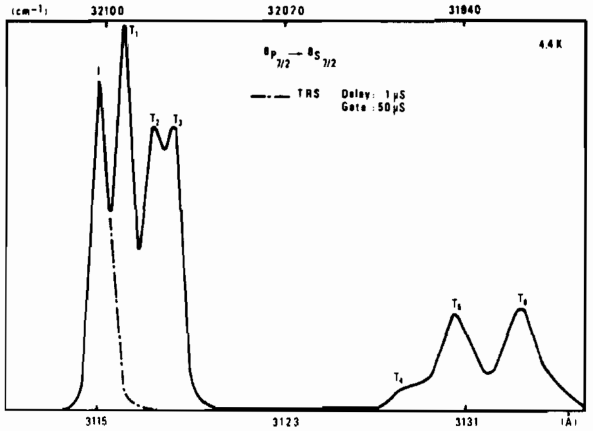

Fig. 4. $^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission spectra of $NaGdF_4$ at 4.4 K: (——) integrated spectrum; (—·—) time-resolved spectrum.

Decay measurements of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ fluorescence show that down to 200 K the decay curve is exponential with a decay time of 1.42 ms, and non-exponential below this temperature, denoting the mentioned energy transfers.

K_2GdF_5

In this compound the Gd^{3+} ion is hepta-coordinated to the fluorides and the GdF_7 polygons form chains along the c axis. The Gd^{3+}–Gd^{3+} distance takes the value of 5.407 Å between the two chains and the value of 3.694 Å inside the chain [3].

At 4.4 K, besides the intrinsic line which corresponds to the lowest energy Stark component, the presence should be noted of lines (Fig. 5) which can be attributed to emission from perturbed Gd^{3+} ions.

At room temperature and down to 20 K, the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ fluorescence decay is exponential with a time constant of 6.7 ms, indicating a slight diffusion (the radiative lifetime in $K_2Gd_{0.02}Y_{0.98}F_5$ at 4.4 K is 9 ms).

Below 20 K the decay becomes non-exponential, while the decay of the trap emission shows a rapid rise then exponential behaviour. The curve can be fitted according to a sum of exponential functions in the case of the intrinsic line.

$$Be^{-t/\tau_f} + Ce^{-t/\tau_s}$$

(with $\tau_f = 3$ ms and $\tau_s = 6.7$ ms).

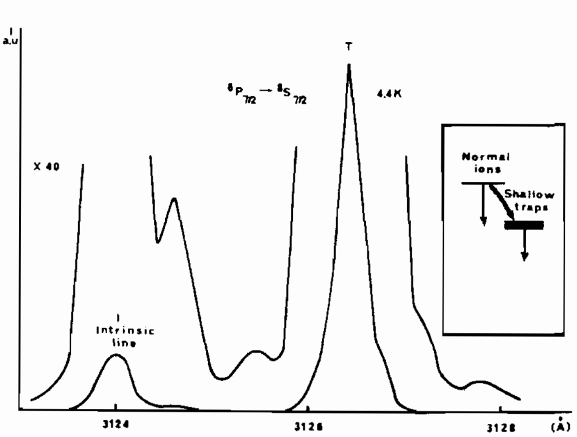

Fig. 5. $^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission spectrum of K_2GdF_5 at 4.4 K.

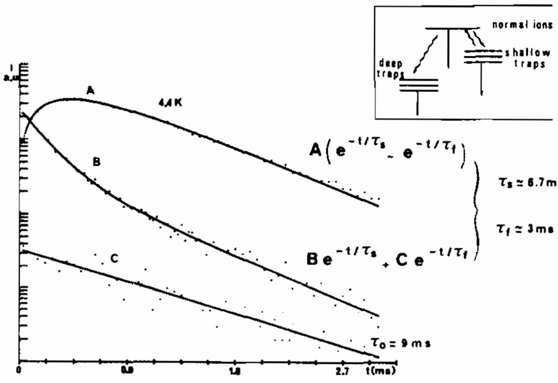

Fig. 6. Fluorescence decays and fits of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition: (A) trap emission (T); (B) intrinsic emission (I); (C) intrinsic fluorescence emission of a diluted phase $K_2Y_{0.98}Gd_{0.02}F_5$.

The same exponential functions allow one to fit the trap decay by

$$A(e^{-t/\tau_s} - e^{-t/\tau_f})$$

according to the model developed by Garapon *et al.* [4]. Experimental points (·) and theoretical fits (solid lines) are shown in Fig. 6. The short-time component corresponds to diffusion and the long-time component comes from thermal back transfers from the traps.

Cubic $RbGd_3F_{10}$

We have already mentioned some Gd^{3+} ion luminescence characteristics in the pure α-$RbGd_3F_{10}$ [1]. The fluorescence decay of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition is exponential down to 77 K with a time constant value of $\tau = 1.38$ ms, differing from the radiative lifetime ($\tau_0 \simeq 5.6$ ms) and indicating an energy transfer between Gd^{3+} ions.

Using the formula $\tau^{-1} = \tau_0^{-1} + 4\pi DC_A \rho$ and the values $\rho = 4.12$ Å for the radius of the sphere of influence and $C_A = 5.4 \times 10^{19}$ ions/cm^3 for the acceptor concentration (impurities), a diffusion constant D is derived as $D = 2 \times 10^{-11}$ cm^2 s^{-1}.

In $RbGd_3F_{10}$ when the alkaline ion is partly replaced by the Eu^{2+} ion, the fluorescence decay of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition for Gd^{3+} is non-exponential. In Fig. 7 the decays obtained for different Eu^{2+} concentrations are shown, the experimental points are plotted as crosses.

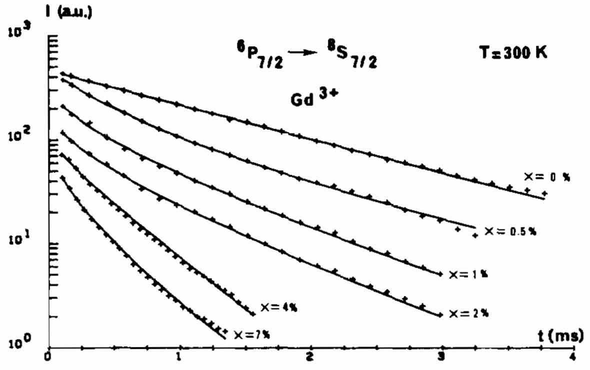

Fig. 7. Decay curves of Gd^{3+} fluorescence *versus* Eu^{2+} concentration (x = at %).

Using Yokota and Tanimoto's equation [5]:

$$I(t) = I_0 \exp(-t/\tau_0) \exp\left[-4/3\pi^{3/2} Na (Ct)^{1/2} \times \left(\frac{1 + 10.87z + 15.5z^2}{1 + 8.743z}\right)^{3/4}\right]$$

(with $z = DC^{-1/3}t^{2/3}$ and Na = acceptor concentration and C = interaction parameter)

we have attempted to fit the experimental decays. This attempt allowed us to obtain the curves drawn (solid lines in Fig. 7). It can be seen that there is good agreement between experimental and theoretical fits. So we conclude that a diffusion-limited energy transfer migration exists. A diffusion constant as well as an interaction parameter have been calculated: $D = 2 \times 10^{-11}$ cm^2 s^{-1}; $C = 7 \times 10^{-39}$ cm^6 s^{-1} at 300 K.

Anti-Stokes Emission

In all of these compounds, anti-Stokes emissions can be observed. We give here the example of K_2GdF_5 where the $^6I_{7/2} \rightarrow {}^8S_{7/2}$ fluorescence is obtained on exciting the $^6P_{7/2}$ level. In Fig. 8 we can see that the fluorescence decay of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition presents a rapid rise followed by an exponential part. At small excitation power (~10^{13} excited ions/cm^3) experimental points can be fitted to a sum of two exponential functions.

$$D(e^{-2t/\tau(^6P_{7/2})} - e^{-t/\tau(^6I_{7/2})})$$

This fit is characteristic of an APTE process [6].

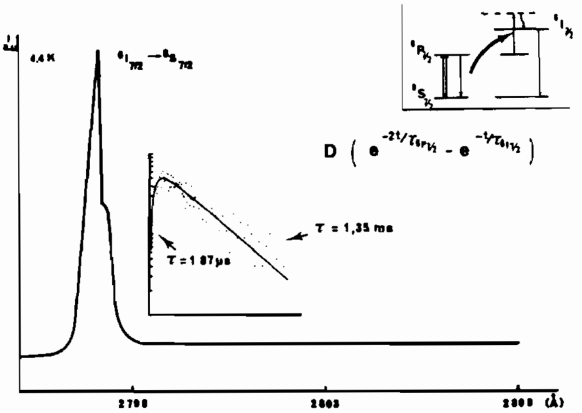

Fig. 8. Anti-Stokes emission spectrum of $^6I_{7/2} \rightarrow {}^8S_{7/2}$ on exciting in the $^6P_{7/2}$ level and intrinsic emission decay curve.

Conclusions

We have reported a study of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission transition in several Gd^{3+} concentrated fluoride compounds in view of the Eu^{2+} host matrices use. In $NaGdF_4$ the presence of two crystallographic sites has been confirmed by optical investigations and also there was evidence of energy migration by a rapid diffusion process at $T > 200$ K. In the case of K_2GdF_5, despite its uni-dimensional crystallographic structure, it appears that an optical excitation trapping by perturbed Gd^{3+} centres or luminescent impurities dominates the fluorescence dynamics at low temperature. Finally, we have proposed a diffusion-limited process for the $Gd^{3+} \rightarrow Eu^{2+}$ energy transfer in cubic $RbGd_3F_{10}$.

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