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ENERGY MIGRATION IN Eu\textsuperscript{3+} COMPOUNDS; ITS DEPENDENCE ON DIMENSIONALITY AND Eu\textsuperscript{3+}-Eu\textsuperscript{3+} DISTANCE

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Abstract - The compound EuAl\textsubscript{3}B\textsubscript{4}O\textsubscript{12} shows thermally activated energy migration among the 5\textsuperscript{D0} excited level. In NaEuTiO\textsubscript{4} this migration reduces to two-dimensional, down to the lowest temperatures, whereas in EuMgB\textsubscript{5}O\textsubscript{10} one-dimensional migration is observed. For short distances and low temperatures the Eu\textsuperscript{3+}-Eu\textsuperscript{3+} transfer occurs by exchange.

I - INTRODUCTION

Energy migration in EuAl\textsubscript{3}B\textsubscript{4}O\textsubscript{12} with a three-dimensional structure and Eu-Eu distance of 5.9 Å has been investigated in our laboratory some years ago /1/. These investigations have now been extended to compounds in which the Eu\textsuperscript{3+} ions occupy lower-dimensional lattices (NaEuTiO\textsubscript{4};2D, EuMgB\textsubscript{5}O\textsubscript{10};1D) and the Eu\textsuperscript{3+}-Eu\textsuperscript{3+} distances are much shorter. Extended reports are published elsewhere /2-6/.

II - EXPERIMENTAL

The reader is referred to Refs./1-6/ for the experimental details.

III - NaEuTiO\textsubscript{4} /2/

The compound NaEuTiO\textsubscript{4} has a layer structure in which the Eu-Eu distance in the layer amounts to 3.7 Å and between the layers 10 Å (Fig.1). Excitation into the Eu\textsuperscript{3+} ions is followed by energy migration among the Eu\textsuperscript{3+} ions. The luminescence output is low, due to efficient trapping of the excitation energy by killer centres (transition-metal ions, mainly iron). This is
Fig. 1 - The crystal structure of NaEuTiO$_4$. Black circles Ti$^{4+}$, open circles O$^{2-}$, hatched circles Na$^+$, dotted circles Eu$^{3+}$.

Fig. 2 - Decay curves of the $^5D_0 - ^7F_2$ Eu$^{3+}$ emission of NaEuTiO$_4$ at 1.2 K and 27.5 K. The fitted curves are discussed in the text.

Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>Eu-Eu distance (Å)</th>
<th>Diffusion constant $(300 \text{ K; cm}^2\text{s}^{-1})$</th>
<th>Hopping time $(300 \text{ K; s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuAl$_3$B$<em>4$O$</em>{12}$</td>
<td>1</td>
<td>5.9</td>
<td>$8 \times 10^{-10}$</td>
<td>$8 \times 10^{-7}$</td>
</tr>
<tr>
<td>NaEuTiO$_4$</td>
<td>2</td>
<td>3.7</td>
<td>$2 \times 10^{-8} \ast$</td>
<td>$2 \times 10^{-8}$</td>
</tr>
<tr>
<td>EuMgB$<em>2$O$</em>{10}$</td>
<td>6</td>
<td>4.0</td>
<td>$\sim 10^{-8}$</td>
<td>$\sim 10^{-7}$</td>
</tr>
</tbody>
</table>

$\ast$ $D = 8 \times 10^{-11}\text{cm}^2\text{s}^{-1}$ at 1.2 K.
even the case at 1.2 K. A small part of the excitation energy is trapped by Eu\textsuperscript{3+} traps. The presence of these traps is due to a slight disorder among the Eu\textsuperscript{3+} and Na\textsuperscript{+} ions. These results show that energy transfer between Eu\textsuperscript{3+} ions at 1.2 K and 3.7 Å separation is possible. Since the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition on Eu\textsuperscript{3+} in NaEuTiO\textsubscript{4} has a certain transition probability, it is not possible to decide on the mechanism which is responsible for the transfer process. Figure 2 shows the decay curves of the intrinsic Eu\textsuperscript{3+} emission of NaEuTiO\textsubscript{4}. These curves do not become exponential after a certain time as was the case for Eu\textsuperscript{3+}Al\textsubscript{2}B\textsubscript{4}O\textsubscript{12} /1/. It was possible to fit the curves to the expression

$$I(t) = I(0) \exp(-p_t t) (4\pi\alpha^2 \Delta t)^{-1}$$

which has been derived for two-dimensional, diffusion-limited energy migration in the limit $t \rightarrow \infty$ /7/. This, together with the structural data (Fig.1), suggests strongly that the energy migration in NaEuTiO\textsubscript{4} is two-dimensional. Table I contains some migration characteristics.

IV - EuMgB\textsubscript{5}O\textsubscript{10} /6/

The crystal structure of EuMgB\textsubscript{5}O\textsubscript{10} contains linear Eu\textsuperscript{3+} chains in which the Eu–Eu distance amounts to 4.0 Å; the distance between the chains is 6.0 Å. The luminescence output of the Eu\textsuperscript{3+} emission of the system Gd\textsubscript{1-x}Eu\textsubscript{x}MgB\textsubscript{5}O\textsubscript{10} increases with $x$ up to $x = 1.0$ at 4.2 K and up to $x = 0.85$ at 300 K. This suggests strongly that at 4.2 K energy migration is of no importance and that at 300 K energy migration occurs, but restricted to one dimension, so that concentration quenching becomes of influence at very high Eu\textsuperscript{3+} concentration only. This quenching is confirmed by the strong killing action of Ni\textsuperscript{2+} (on Mg\textsuperscript{2+} sites) and Na\textsuperscript{3+} (on Eu\textsuperscript{3+} sites) on the 300 K luminescence intensity of EuMgB\textsubscript{5}O\textsubscript{10}. The one-dimensional character of the energy migration is confirmed by decay measurements. The latter show that at 4.2 K one-step transfer to killers and Eu\textsuperscript{3+} traps prevails. At higher temperatures, however, the migration becomes effective. Its temperature dependence can be analyzed and occurs to be due to phonon assistance: below 50 K a $T^3$ dependence is observed (two-phonon assistance), at higher temperatures an $\exp(-E_{01}/kT)$ dependence with $E_{01}$ the energy difference between the $^7\text{F}_0$ level and the lowest $^7\text{F}_1$ level. Of main importance is that all decay curves can be fitted to the expression

$$I(t) = I(0) \exp(-p_t t - Bt^{1/3})$$

Fig. 3 - Decay curve of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ Eu\textsuperscript{3+} emission of EuMgB\textsubscript{5}O\textsubscript{10}:0.1% Na\textsuperscript{3+} at 130 K. The fitted curve is discussed in the text.
indicating one-dimensional energy migration (see Fig. 3). The concentration dependence of the luminescence output suggests $P_{\text{intra}} > P_{\text{rad}} > P_{\text{inter}}$, where the P's denote the probabilities for transfer between Eu$^{3+}$ in the chain, radiative Eu$^{3+}$ decay and transfer between Eu$^{3+}$ in different chains, respectively. We found $P_{\text{rad}}$ to be $350 \text{ s}^{-1}$ and estimated $P_{\text{intra}}$ to be about $10^7 \text{ s}^{-1}$ (see also Table 1). This yields $P_{\text{intra}} < 10^2 \text{ s}^{-1}$. The Eu$^{3+}$-Eu$^{3+}$ transfer probability decreases therefore with a factor $> 10^5$ when the distance increases from 4.0 to 6.0 Å. This pronounced distance dependence points strongly to an exchange-mediated transfer.

V - Eu$_2$Ti$_2$O$_7$ /5/

To demonstrate the existence of exchange interaction between Eu$^{3+}$ ions further, we investigated the pyrochlore Eu$_2$Ti$_2$O$_7$. In this structure the Eu$^{3+}$ ions occupy sites with inversion symmetry. In this way the $^5D_0 - ^7F_0$ transition is forbidden completely, so that transfer by multipoles will vanish at low temperatures. On the other hand the Eu$^{3+}$-Eu$^{3+}$ distance in Eu$_2$Ti$_2$O$_7$ is 3.6 Å which makes transfer by exchange well possible. Unfortunately a slight disorder in Eu$_2$Ti$_2$O$_7$ induces a rather large amount of Eu$^{3+}$ ions which feel an effectively lower symmetry without an inversion centre. Nevertheless it was possible to show that energy migration among the Eu$^{3+}$ ions occurs down to the lowest temperatures which is another strong indication that the Eu$^{3+}$-Eu$^{3+}$ transfer occurs by exchange. In EuAl$_2$B$_4$O$_{12}$ the Eu-Eu distance is obviously too long (5.9 Å) to allow energy transfer by exchange interaction at low temperatures. Transfer is only possible via thermal population of the $^7F_1$ level. In conclusion we have demonstrated three-, two-, and one-dimensional energy migration for one and the same system of ions, viz. Eu$^{3+}$. The contribution of exchange interaction to the transfer steps involved must be considerable if the Eu-Eu distance is not too long.

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REFERENCES