ENERGY MIGRATION IN ONE-DIMENSIONAL $Li_6Eu(BO_3)_3$

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Analysis of the luminescence properties of Eu^{3+} in $Li_6Eu(BO_3)_3$ suggests that the energy migration which occurs over the Eu^{3+} sublattice down to low temperatures is one-dimensional. The temperature dependence of the migration points to a two-site non-resonant two-phonon assisted process. It occurs by exchange interaction.

1. Introduction

Numerous theoretical and experimental studies have been undertaken on the migration of optical excitations in one-dimensional systems (see e.g. refs. [1,2] and references therein). Experimental work has mostly focused on molecular crystals and Mn^{2+} compounds. In our laboratory attention has been directed to $LnMgB_5O_{10}$ – an inorganic solid with a one-dimensional rare-earth sublattice – and the energy migration processes in the Gd^{3+} [3], Eu^{3+} [4] and Tb^{3+} [5] compounds were studied. It appeared that the energy migration was one-dimensional in $EuMgB_5O_{10}$, quasi-one-dimensional in $TbMgB_5O_{10}$ and three-dimensional in $GdMgB_5O_{10}$.

Garapon et al. [6] investigated the energy migration in the Gd^{3+} compound of another borate with a one-dimensional sublattice, viz. $Li_6Ln(BO_3)_3$. They found indirect evidence for one-dimensional migration, changing into three-dimensional below 40 K. Our previous work showed that the dimensionality of the sublattice was reflected more in the Eu^{3+} compound than in the Gd^{3+} compound. One would expect this finding to apply to $Li_6Ln(BO_3)_3$ also, since the 4f electrons involved in the energy transfer processes are well shielded from the crystalline environment by the 5s and 5p electrons, and the energy transfer distances in $Li_6Ln(BO_3)_3$ are similar to those in $LnMgB_5O_{10}$ (3.9 Å inside the Ln^{3+} chain and 6.7 Å between the Ln^{3+} chains for the former, compared to 4.0 and 6.0 Å, respectively, for the latter). To

investigate this we carried out luminescence measurements on powder samples of undoped $Li_6Eu(BO_3)_3$, on $Li_6(Gd,Eu)(BO_3)_3$ where the Eu^{3+} sublattice is diluted with Gd^{3+} which acts as a scattering impurity for the Eu^{3+} excitations, and on $Li_6Eu(BO_3)_3$ doped with Nd^{3+}, which is an acceptor of the Eu^{3+} excitation.

2. Experimental

The powder samples of $Li_6Gd_{1-x}Eu_x(BO_3)_3$ $(0 < x \leqslant 1)$ were prepared by firing an intimate mixture of Gd_2O_3 (Highways, 99.999%), Eu_2O_3 (Highways, 99.99%), Li_2CO_3 (excess, Merck, p.a. grade) and H_3BO_3 (excess, Merck, p.a. grade) at 750°C in air for several hours. For the incorporation of small amounts of Nd^{3+} (varying from 0.01% to 0.3%) into $Li_6Eu(BO_3)_3$, Eu_2O_3 and Nd_2O_3 (Highways, 99.999%) were dissolved in nitric acid (Merck, p.a. grade). After addition of the correct amount of Nd^{3+} solution to the Eu^{3+} solution, it was evaporated to dryness. Both methods of preparation led to the same crystallographic results, as was checked by X-ray powder diffraction.

The experimental apparatus has been described in refs. [4,7].

3. Results and discussion

3.1. Spectral properties

For an analysis of the energy transfer processes in a given compound, it is necessary to know its luminescence properties. The emission spectrum at 4.2 K of $Li_6Eu(BO_3)_3$ after excitation into the $^5L_6$ levels is shown in fig. 1. The positions of the $^5D_0 \rightarrow ^7F_{0,1}$ transitions are given in table 1. The number of lines agrees with the C_1 site symmetry of the Eu^{3+} ion in $Li_6Eu(BO_3)_3$. The emission occurs from the $^5D_0$ level only, due to efficient multiphonon relaxation from the higher ^5D levels to the $^5D_0$ level. Vibronic sidebands in the excitation spectrum reveal that vibrations with energies up to 1300 cm^{-1} (asymmetric BO_3^{3-} stretching) are present in this compound.

Following site-selective excitation a whole series

Table 1
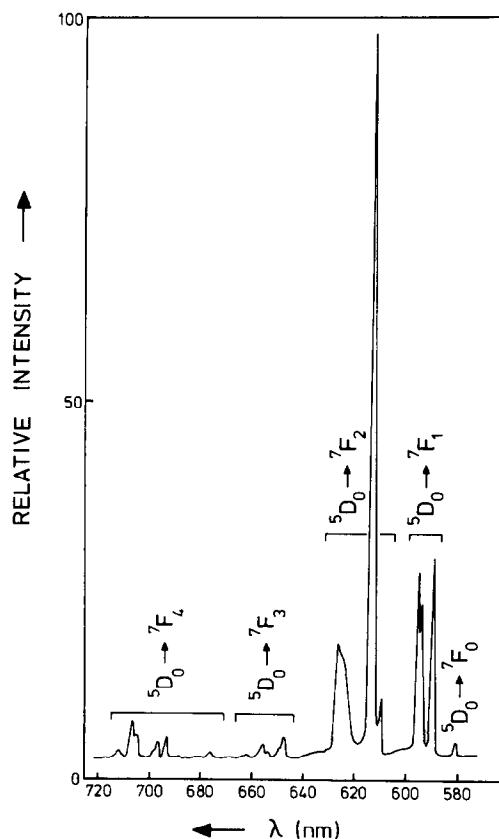Positions of the $^5D_0 \rightarrow ^7F_{0,1}$ transitions in $Li_6Eu(BO_3)_3$

Transition	λ (nm)	E (cm^{-1})
$^5D_0 \rightarrow ^7F_0$	580.11	17238
$^5D_0 \rightarrow ^7F_1$	588.82	16983
	593.58	16847
	594.95	16808

of weak emission peaks different from those in fig. 1 are found. These peaks belong to Eu^{3+} ions on non-regular crystallographic sites, a commonly observed phenomenon in Eu^{3+} compounds [4,7]. At least two types of non-regular ions can be distinguished in $Li_6Eu(BO_3)_3$. The excitation spectra of these ions show that there is energy transfer at 4.2 K from the regular to the non-regular Eu^{3+} ions, which thus act as traps for the excitation energy. The trap depths of the two most prominent non-regular ions can be determined from the position of the $^5D_0 \rightarrow ^7F_0$ transition to be 3 and 8 cm^{-1}. Garapon et al. [6] found ten types of non-regular Gd^{3+} ions in a $Li_6Gd(BO_3)_3$ crystal, with trap depths up to 86 cm^{-1}. Due to this large depth these non-regular ions play an important role in the energy migration process in $Li_6Gd(BO_3)_3$. The role of the non-regular Eu^{3+} ions in $Li_6Eu(BO_3)_3$ will be considered below.

Another feature of interest in the analysis of the energy migration is the dependence of the integrated ($^5D_0 \rightarrow ^7F_{0-4}$) emission intensity as a function of the Eu^{3+} concentration x in $Li_6Gd_{1-x}Eu_x(BO_3)_3$. This is given in fig. 2. At 300 K concentration quenching occurs above $x = 0.85$, which indicates that above this concentration the excitation energy can migrate over the Eu^{3+} sublattice to quenching sites [4,7]. Fig. 2. also contains results for samples of composition $Li_6Eu_{1-y}Nd_y(BO_3)_3$ ($0.01\% \leqslant y \leqslant 0.3\%$). The enhanced quenching effect of the dopant illustrates that Nd^{3+} acts as an acceptor of the Eu^{3+} excitation. The most important feature of fig. 2 is the fact that the quenching occurs above a Eu^{3+} concentration of 0.85, which is very high. It indicates that the energy migration is restricted to the one-dimensional Eu^{3+} chains, since a decrease in dimensionality reduces the probability that the migrating excitation encounters one of the randomly distributed quenching sites [8]. In two- and three-dimensional Eu^{3+} compounds concentration quenching was found to occur
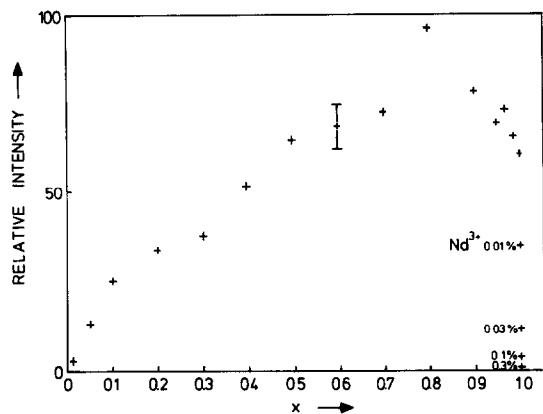

Fig. 1. Emission spectrum of $Li_6Eu(BO_3)_3$, recorded at 4.2 K ($\lambda_{exc} = 395$ nm).

Fig. 2. Concentration dependence of the integrated Eu^{3+} emission intensity of $Li_6Gd_{1-x}Eu_x(BO_3)_3$ and $Li_6Eu_{1-x}Nd_x(BO_3)_3$ at 300 K ($\lambda_{exc}=395$ nm).

Fig. 3. Semilogarithmic decay curve of the Eu^{3+} $^5D_0$ emission ($\lambda_{em}=588.82$ nm, $\lambda_{exc}=465.33$ nm) in $Li_6Eu_{0.999}Nd_{0.001}(BO_3)_3$, recorded at 40 K. Solid line: fit to eq. (1).

above $x=0.3$ [7,9], while a critical concentration of 0.85 was found in the one-dimensional $EuMgB_5O_{10}$ compound [2,4].

3.2. Time dependence of the luminescence

A detailed analysis of the $^5D_0$ Eu^{3+} emission decay was carried out in order to obtain a quantitative description of the energy migration in $Li_6Eu(BO_3)_3$. The radiative decay time was determined to be 2.5 ms, using a sample of composition $Li_6Gd_{0.99}Eu_{0.01}(BO_3)_3$, where no energy transfer occurs due to the low Eu^{3+} concentration. This value is in agreement with the value of 2.3 ms found by Garapon et al. [6].

The shape of the Eu^{3+} decay curve in the $Li_6Eu(BO_3)_3:Nd^{3+}$ samples (including the $Li_6Eu(BO_3)_3$ sample) depends on temperature and on Nd^{3+} concentration. At 4.2 K the curve comprises a non-exponential initial part, which is due to direct transfer from the regular Eu^{3+} ions to acceptors, viz. the non-regular ions, the quenching sites and the Nd^{3+} ions, and an exponential long-time part. The decay time of this part is slightly smaller than the radiative decay time, which means that some energy migration already occurs in the concentrated Eu^{3+} compound at this temperature. The decay rate of the long-time increases with increasing temperature and the long-time part becomes increasingly more non-exponential. An example of such a decay curve is given in fig. 3. This behaviour is the more
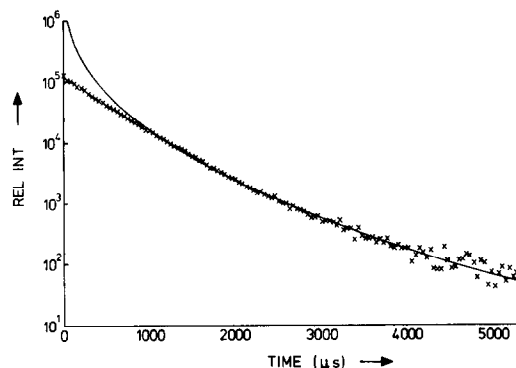
pronounced the higher the Nd^{3+} concentration in the sample is. It can be explained by the fact that a thermally assisted energy migration process occurs over the Eu^{3+} sublattice to the acceptors. This leads to an increase in the decay rate with increasing temperature, a commonly observed phenomenon in concentrated Eu^{3+} systems [2,7,9–12]. The non-exponential behaviour indicates that this energy migration is not three-dimensional, because in that case an exponential long-time decay, faster than the radiative decay, is expected [13]. Above 90 K the shape of the decay curve does not change significantly.

In view of the fact that the non-regular Eu^{3+} ions, which are present in a very small concentration since their emission lines do not appear in fig. 1, are thermalized with respect to the regular Eu^{3+} ions in the temperature range in which the migration occurs, we will neglect them as acceptors for the energy migration. Movaghar et al. [14] have derived an expression for the long-time development of the donor luminescence intensity in the case of energy migration over a one-dimensional system of donor sites, with randomly distributed acceptors of infinite trap depth. This is

$$I(t) \propto \exp(-t/\tau_0 - Bt^{1/3}) , \tag{1}$$

with

$$B=3(\tfrac{1}{4}\pi^2 x_a^2 P)^{1/3} , \tag{2}$$

where τ_0 is the radiative decay time, x_a the acceptor concentration and P the donor–donor transfer probability. It appears that all the Eu^{3+} $^5D_0$ decay curves

can be fitted in a very satisfactory way to eq. (1). This is another indication that we are dealing with one-dimensional energy migration. The long-time part has been interpreted as the region where $I(t) <$ $0.01I(0)$ [15]. An example of such a fit is given by the solid line in fig. 3.

The temperature dependence of the migration process stems from the inhomogeneous broadening of the $^5D_0 \leftrightarrows {}^7F_0$ transition [4,7]. The linewidth of this transition is 3.5 cm^{-1} in $Li_6Eu(BO_3)_3$ at 4.2 K, which exceeds the homogeneous linewidth (less than 1 cm^{-1} at these temperatures [16]). The energy mismatches between the $^5D_0$ levels of regular Eu^{3+} ions can be overcome by phonon assistance which is a strongly temperature-dependent process. At about 140 K the linewidth of the $^5D_0 \rightarrow {}^7F_0$ transition starts to increase towards its value of 4.5 cm^{-1} at 300 K. Although this increase is on the edge of the resolution of our equipment it indicates that the homogeneous, temperature-dependent broadening dominates the inhomogeneous temperature-independent broadening at these temperatures. This will reduce the energy mismatches between the Eu^{3+} ions, which is probably responsible for the fact that the energy migration rate remains constant above 90 K.

The nature of the phonon assistance can be derived from the temperature dependence of the donor-donor transfer probability P. Since the exact number of quenching centers which determine x_a in eq. (2) is unknown we have to use the temperature dependence of the fit parameter B^3. This has the same temperature dependence if we make the obvious assumption that x_a is temperature independent. It appears that for all the $Li_6Eu(BO_3)_3:Nd^{3+}$ samples the parameter B^3 increases with T^3, indicating a two-site non-resonant two-phonon assisted process [17]. This process is commonly encountered in rare-earth compounds [4,10,18]. An illustration is given in fig. 4 for a sample of composition $Li_6Eu_{0.999}Nd_{0.001}(BO_3)_3$. The solid line is given by

$$B^3 = c_1 T^3, \tag{3}$$

where the fit parameter c_1 is equal to 1.78 s^{-1} K^{-3}. It depends, among other things, on the transverse velocity of sound in this compound and the difference in ion-phonon coupling strengths between the ground and excited states of the Eu^{3+} ions involved.

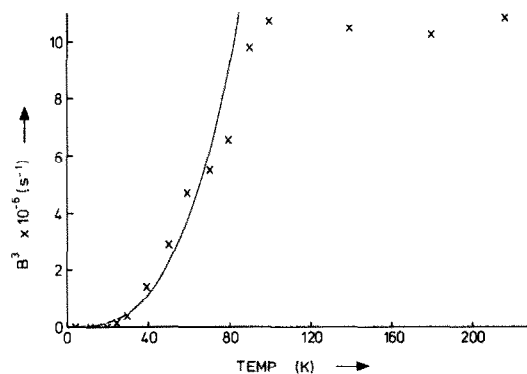Fig. 4. Temperature dependence of B^3 for $Li_6Eu_{0.999}$ $Nd_{0.001}$-$(BO_3)_3$. Solid line: fit to eq. (3).

Since no further data are available on $Li_6Eu(BO_3)_3$, it cannot be evaluated.

If one assumes that the amount of concentration quenching in $Li_6Eu(BO_3)_3$, with and without Nd^{3+} dopes, as given in fig. 2, scales with the total amount of quenching centers and Nd^{3+} concentration, one can obtain an estimate of the percentage of quenching centers in the undoped $Li_6Eu(BO_3)_3$ by extrapolating the data in fig. 2. This leads to a value of 0.008% which is low compared to that found in $EuMgB_5O_{10}$, viz. 0.5% [4]. The use of this value in eq. (2), where $x_a = 0.008\% + x_{Nd^{3+}}$, together with the fit parameters B for the different $Li_6Eu(BO_3)_3$ samples, leads to a donor–donor transfer probability of 10^7 s^{-1} at 300 K, which is the same as in $EuMgB_5O_{10}$ [4]. This is satisfactory, since the interchain separation between Eu^{3+} ions is nearly the same for both compounds (3.9 versus 4.0 Å).

For the latter compound it was argued that the energy transfer has to occur by exchange interaction. If we assume that this holds also for $Li_6Eu(BO_3)_3$, we get a probability for transfer between two neighbouring Eu^{3+} ions on different chains (separation 6.7 Å) of 10^{-1} s^{-1}, using the distance dependence of the exchange interaction (equal to $\exp(-2R/L)$, where R is the separation and L an effective average Bohr radius for the excited and unexcited states, which can be taken to be 0.3 Å for Eu^{3+} [19]). In the case of multipolar interaction (which has a distance dependence of R^{-s}, where $s = 6, 8, 10, \dots$ for electric dipole–dipole, dipole–quadrupole, quadrupole–quadrupole, ... interaction) this interchain

probability becomes 4×10^5 s^{-1}, 10^5 s^{-1} and 5×10^4 s^{-1} for $s = 6$, 8 and 10, respectively, which is much larger than the radiative decay rate of 400 s^{-1}. Therefore, one would expect the energy migration not to be one-dimensional in the case of multipolar interaction.

In conclusion, the energy migration in $Li_6Eu(BO_3)_3$ behaves in the same way as in $EuMgB_5O_{10}$, both compounds having a one-dimensional Eu^{3+} sublattice.

Acknowledgement

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