NON-RADIATIVE RELAXATION OF THE Eu^{3+} $^5D_1$ LEVEL IN $NaGdTiO_4$

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Non-radiative relaxation by multi-phonon emission has been investigated for the $^5D_1$ level of Eu^{3+} in $NaGdTiO_4$. The $^5D_1 \rightarrow {}^5D_0$ relaxation rate has been evaluated in the temperature region between 4.2 K and room temperature. The temperature dependence of the relaxation rate points to a fifth-order process. The frequency of the emitted phonons corresponds with that of the Gd–O stretching vibrations.

1. Introduction

Non-radiative relaxation between electronic states of rare-earth ions in solids occurs by the emission of phonons. The theory has been described extensively [1–6]. The critical factor in the multi-phonon relaxation process is the number of phonons required to conserve energy. The frequency of each of the emitted phonons should be close to the maximum frequency in the phonon spectrum, since such a process involves the smallest number of phonons and has the highest probability [5]. This has been confirmed experimentally. However, if lower-frequency modes are more numerous and strongly coupled, the dominant process may occur in higher order (see, for example, ref. [7]).

The $^5D_1 \rightarrow {}^5D_0$ relaxation of Eu^{3+} has been studied in a number of compounds [6–8]. The rate was found to be abnormally slow. This is due to the only selection rule observed in multi-phonon relaxation, viz. between levels with $J = 0$ and $J = 1$ [9]. We investigated the $^5D_1 \rightarrow {}^5D_0$ relaxation properties of Eu^{3+} in powdered samples of $NaGdTiO_4$: Eu^{3+} (1%) using selective-excitation and time-resolved spectroscopy. The crystal structure of $NaGdTiO_4$ is described in ref. [10]. The luminescence properties of $NaGdTiO_4$: Eu^{3+} were investigated by Blasse and Bril [11] and by Linarès and Blanchard [12]. Recently, we investigated the energy-transfer phenomena in $NaEuTiO_4$ [13].

Both decay curves of the $^5D_1$ and the $^5D_0$ emission were recorded upon laser excitation in $^5D_1$. The temperature dependence of the $^5D_1 \rightarrow {}^5D_0$ relaxation rate can be explained by a fifth-order multi-phonon process, as shown below.

2. Experimental

The preparation of the powdered samples was described in ref. [12]. For the low-temperature measurements, the samples were immersed into liquid helium in a Thor bath cryostat (S-100). The temperature of the samples could be regulated between 4.2 K and room temperature. For measuring the emission spectra, a tunable dye laser (Molectron DL200) pumped with a nitrogen laser (Molectron UV14) was used as an excitation source. The laser generated a pulse with a peak power of 30 kW and a width of about 10 ns. The repetition rate was set at 40 Hz. The resolution of this equipment amounts to 1 cm^{-1}. The emission was detected using a Spex 1704x high-resolution monochromator in combination with a cooled photomultiplier (RCA type C31034). To record the time-resolved spectra and the decay of the luminescence, a PAR model 162/165 boxcar averager was used.

3. Results

The emission and excitation spectra of the Eu^{3+} luminescence in $NaGd_{0.99}Eu_{0.01}TiO_4$ were presented in refs. [12,13]. We used a tunable dye laser to excite selectively the lowest-lying $^5D_1$ level (at 18941 cm^{-1}).
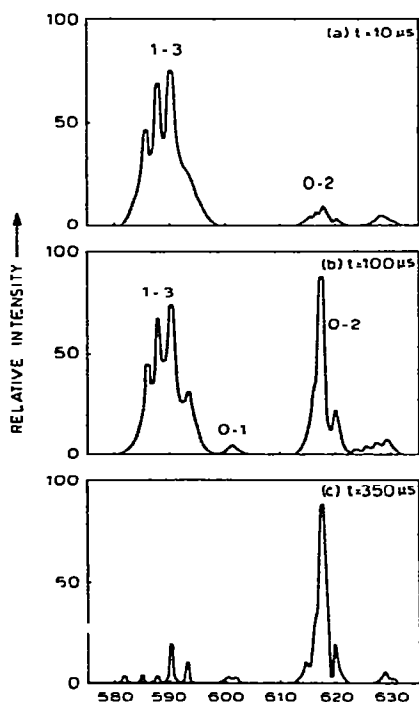
Fig. 1. The time dependence of the emission spectrum of Eu^{3+} in $NaGd_{0.99}Eu_{0.01}TiO_4$ upon excitation in $^5D_1$ at 4.2 K. t indicates the time after the excitation pulse. The notation $J - J'$ refers to the transitions $^5D_J - {}^7F_{J'}$.

To monitor the relaxation from $^5D_1$ to $^5D_0$, we measured emission spectra at 4.2 K as a function of time in the range 10–350 μs after the excitation pulse. Fig. 1 shows the time dependence of the $^5D_1 \rightarrow {}^7F_3$ and the $^5D_0 \rightarrow {}^7F_1$, $^7F_2$ emission spectra of the Eu^{3+} ions. The spectrum recorded 10 μs after the laser pulse shows mainly the $^5D_1 \rightarrow {}^7F_3$ emission (around 590 nm). However, the $^5D_0 \rightarrow {}^7F_2$ emission around 617 nm can be recognized. The spectrum recorded 100 μs after the pulse shows a relative decrease of the emission from $^5D_1$. This effect becomes even more drastic at 350 μs after the excitation pulse, as can be seen in fig. 1c. This spectrum resembles the time-integrated emission spectrum recorded at 4.2 K with excitation in $^5D_1$.

The decay characteristics of the $^5D_1$ and the $^5D_0$ emission upon excitation in $^5D_1$ were investigated as a function of temperature. For the former, the decay curves are exponential in the whole temperature region under study. The decay curves of the emission from
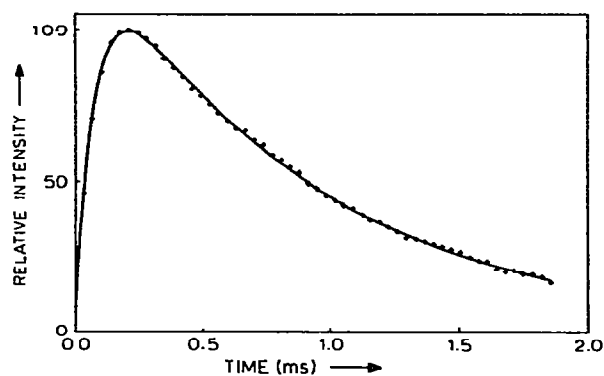
Fig. 2. Decay curve of the $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} in $NaGd_{0.99}Eu_{0.01}TiO_4$ at 4.2 K.

$^5D_0$ show a build-up. This is illustrated in fig. 2, which shows the decay curve of the $^5D_0$ emission at 4.2 K upon $^7F_0 \rightarrow {}^5D_1$ excitation. The decay curves are exponential for long times after the pulse. The plotted line in fig. 2 is a theoretical fit, as discussed below.

4. Discussion

There are several methods of obtaining the $^5D_1 \rightarrow {}^5D_0$ relaxation rate. We calculated the relaxation rate with three different methods. The calculated values were in good agreement with each other. Consider the simple three-level ($^5D_1 > {}^5D_0 > {}^7F$) scheme of fig. 3. Neglecting thermal population of level 2 and
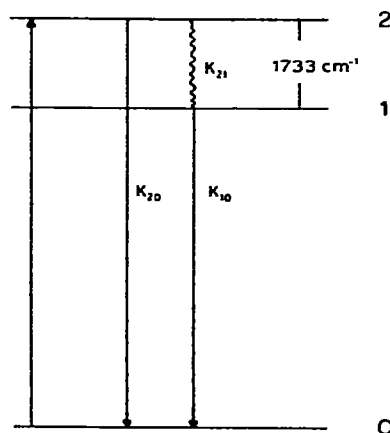

Fig. 3. Three-level scheme used in the calculations.

non-radiative transitions to level 0. the rate equations for the populations of levels 1 and 2 after excitation in level 2 are:

$$dn_2/dt = -k_{21}n_2 - k_{20}n_2 , \qquad (1)$$

$$dn_1/dt = k_{21}n_2 - k_{10}n_1 . \qquad (2)$$

The solution of eqs. (1) and (2) for the population of level 1 at time t after the excitation pulse is

$$n_1 = A\{\exp(-k_{10}t) - \exp[-(k_{21} + k_{20})t]\} . \qquad (3)$$

It can easily be shown (see, for example, ref. [14]) that for the simple case where level 2 relaxes to an emitting level 1. the emission from level 1 will exhibit a maximum intensity at time

$$t_{max} = \ln(K_1/K_2)/(K_1 - K_2) . \qquad (4)$$

Here K_1 and K_2 are the summations of all possible radiative and non-radiative probabilities from level 1 and level 2, respectively. Integration of eqs. (1) and (2) yields the intensities of the emission from levels 2 and 1 under continuous excitation in level 2. The ratio of the intensities is given by

$$I_2/I_1 = k_{20}/k_{21} . \qquad (5)$$

We calculated the relaxation rate k_{21} by using eqs. (3), (4) and (5). The required data were obtained from the $^5D_0 \to {}^7F_J$ decay curves and the time-integrated emission spectra. Since the ratio of the $^5D_1$ and the $^5D_0$ emission intensities of $NaGd_{0.99}Eu_{0.01}TiO_4$ and $NaGd_{0.95}Eu_{0.05}TiO_4$ are nearly the same, neglect of cross relaxation as a process which contributes to the $^5D_1 - {}^5D_0$ relaxation in our 1% Eu^{3+} sample can be justified. For the relaxation rate at 4.2 K we obtain $k_{21} = 13.2 \times 10^3$ s^{-1} from a computer fit of the experimental decay curve using eq. (3). The theoretical fit is shown in fig. 2. Using eq. (4) we obtain k_{21} $= 13.4 \times 10^3$ s^{-1}. From the ratio of the intensities we found a value of 12.6×10^3 s^{-1}. A comparison with values of $k_{21} = 2 \times 10^4$ s^{-1} at 4.2 K in YVO_4 [7], $k_{21} = 1.5 \times 10^4$ s^{-1} at 4.2 K in $YAsO_4$ [7] and 1.5×10^4 s^{-1} at 77 K in $YAlO_3$ [8] shows that our value is quite acceptable.

Fig. 4 shows the temperature dependence of the relaxation rate, which was calculated from the computer fits of the $^5D_0 \to {}^7F_J$ decay curves. The theoretical fit is discussed below. The temperature dependence of the multi-phonon relaxation rate has been de-
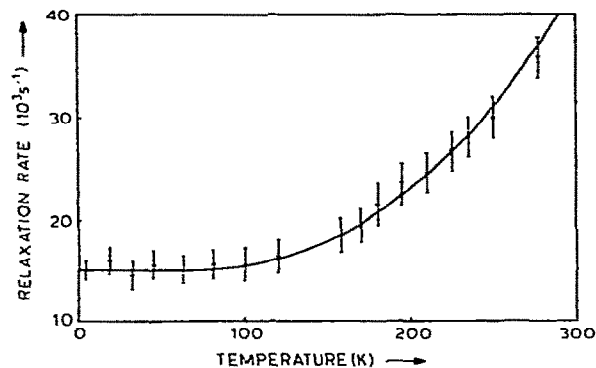

Fig. 4. Temperature dependence of the $^5D_1 - {}^5D_0$ relaxation rate in $NaGd_{0.99}Eu_{0.01}TiO_4$.

scribed by Riseberg and Moos [1]. The number of phonons p of equal energy $\hbar\omega$ required to conserve energy, and hence the order of the process, is determined by the condition

$$p\hbar\omega = \Delta E . \qquad (6)$$

It can be easily shown that the temperature-dependent relaxation rate for a single-frequency p-phonon process becomes

$$k_{21}(T) = k_{21}(0)\{\exp(\hbar\omega/kT)/[\exp(\hbar\omega/kT) - 1]\}^p . \qquad (7)$$

The significance of eq. (7) is in the possibility of establishing the order of the relaxation process and the energies of the dominant phonons involved. We have fitted our experimental data to eq. (7) under the condition that $p\hbar\omega = 1733$ cm^{-1}. The best fit is presented in fig. 4 and was obtained by assuming a fifth-order process (i.e. $p = 5$). The corresponding phonon energy is 347 cm^{-1}.

The infrared and Raman spectra of $NaGdTiO_4$ were presented by Blasse and van den Heuvel [15]. From these spectra it is obvious that the maximum phonon energy is 880 cm^{-1}, corresponding to the TiO_6 symmetric stretching mode. As stated above. the frequency of the emitted phonons is expected to be close to the maximum frequency in the phonon spectrum. However, if lower-frequency modes are more strongly coupled, the dominant process may occur in higher order. The Raman spectrum of $NaGdTiO_4$ shows a peak at 345 cm^{-1}. This peak cannot be ascribed to the internal modes of the TiO_6 octahedron and is probably

due to lattice modes corresponding to Gd(Eu)—O stretching vibrations. This explains the fact that these phonons are strongly coupled.

Acknowledgement

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ERRATUM

A. Castellan, J.-P. Desvergne, R. Lesclaux and J.-C. Soulignac, New insight into fluorescence properties of 1,2-bis(9-anthryl)ethanes: temperature dependence and conformational effects in dilute methylcyclohexane solutions, Chem. Phys. Letters 106 (1984) 117.

On page 122, the equation giving α is incorrect. It should read:

$$\alpha = (\phi_F - \phi_{FG})/(\phi_{FA} + \phi_{FG}\phi_{GA} - \phi_{FG}),$$

where $\phi_{GA} = k_G \tau_1$. This does not modify the following conclusion.