Determination of homogeneous spectral widths by fluorescence line narrowing in $Ca(PO_3)_2:Eu^{3+}$

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Homogeneous spectral widths are determined for inhomogeneously broadened transitions of the Eu^{3+} ion in $Ca(PO_3)_2$ glass by observing resonance fluorescence lines under monochromatic dye-laser excitation. A Lorentzian profile of the emission line measured is consistent with the existing theory. Effects of spectral diffusion and strain broadening on the fluorescence narrowing are discussed.

We wish to report measurements of the spectral shape and width of the fluorescence line of the Eu^{3+} ion in $Ca(PO_3)_2$ whose frequency coincides with that of the monochromatic exciting light. This experiment makes it possible, for the first time in a solid, to determine directly the homogeneous spectral widths of inhomogeneously broadened transitions. The narrow width of 3 cm^{-1} thus obtained for the $^7F_0$-$^5D_0$ transition at room temperature gives evidence for the weakness of the interaction between the Eu^{3+} ion and this amorphous host lattice. Relaxation mechanisms are inferred from the temperature dependence of the resonance fluorescence linewidths. Contribution of inhomogeneous broadening in a narrowed nonresonant emission line is also verified.

In recent years, laser-induced fluorescence line-narrowing experiments have been performed on various solids containing magnetic ions.[1-6] In these experiments, monochromatic-light excitation is made into an excited level resonantly and narrowed fluorescence lines are observed. As is well known, the ligand-field potential acting on magnetic ions in solids usually has several components, so that the effects of microscopic strains on the level energies are complicated and different among various levels. Therefore, great care is indispensable in the interpretation of the narrowed fluorescence linewidths in the nonresonant case where at least three energy levels are concerned with the absorption-fluorescence cycle. On the contrary, in the resonant case where the fluorescence line coincides in frequency with the exciting light, the emission linewidth manifests the homogeneous width of the transition, provided that the spectral diffusion is negligible and that the exciting light is sufficiently monochromatic and weak. Szabo[1] observed resonance fluorescence line narrowing in ruby, but in his experiment the monochromaticity of the exciting laser light or the instrumental resolution was not sufficient to determine the homogeneous linewidth. Further, as will be discussed later, the spectral diffusion is not considered to be negligible in his case. In the present paper, we report an observation of narrowed resonance fluorescence lines whose widths are determined solely by homogeneous broadening mechanisms and accordingly give the (homogeneous) transverse relaxation times.

Let us consider an inhomogeneously broadened absorption line in a solid whose spectral shape is written

$$S(\nu) = \int g(\nu_i) f(\nu_i, \nu)\, d\nu_i \quad , \tag{1}$$

where $f(\nu_i, \nu)$ is the homogeneous line shape, the statistical distribution of the center frequency ν_i being described by the function $g(\nu_i)$. Under monochromatic-light excitation at the frequency ν_l within the absorption line, we expect narrowed resonance fluorescence line because only the centers having the same energy (within the homogeneous width) as the exciting photon are selectively excited. When the spectral diffusion is absent, the spectral shape of this resonance fluorescence line is expressed as

$$F(\nu) = \int g(\nu_i) f(\nu_i, \nu_l) f(\nu_i, \nu)\, d\nu_i \quad . \tag{2}$$

Here, we have assumed that the excitation intensity is weak enough so that the saturation of the absorption is negligibly small. At high temperatures such as 300 K, the homogeneous width of a zero-phonon line is usually dominated by one-phonon direct process and two-phonon Raman scattering.[7] The latter causes Lorentzian-shape line broadening, while the former gives asymmetric Lorentzian, the asymmetry being reduced with the decrease of the linewidth.[8] If we assume that $f(\nu_i, \nu)$ is a Lorentzian with the width $\Delta\nu$ much narrower than the inhomogeneous breadth, $F(\nu)$ reduces to a Lorentzian with the width $2\Delta\nu$. Thus, it is possible to determine homogeneous width in an inhomogeneously broadened line from the breadth of the resonance line under monochromatic-light excitation.

Spectral diffusion due to radiative- and nonradiative-energy transfers among centers gives an important effect on this type of experiment. Namely, resonance transfers that occur via the spectral overlap between the absorption and the narrowed

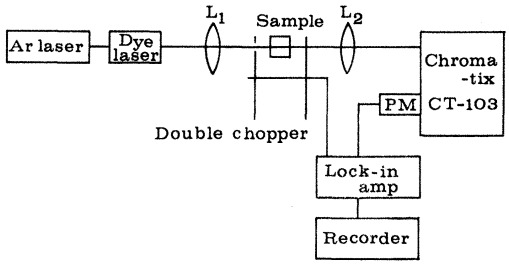

FIG. 1. Experimental setup for the measurement of fluorescence spectra under monochromatic-light excitation.

resonance fluorescence are considered to increase the width of the narrowed resonance line by $2\Delta\nu$ in a time $t = W_T^{-1}$, where W_T is the rate of the energy transfer. Similarly, radiation trapping[9] due to self-absorption of the resonance fluorescence may broaden the line by $2\Delta\nu$ in a time $t = \tau\tau'/(\tau' - \tau)$, where τ' and τ are the fluorescent-decay times with and without self-absorption, respectively. It is well known that the decay time of the R_1 emission in ruby is prolonged very much on account of the trapping at low temperatures.[9] Consequently, the spectral diffusion due to this effect is considered to be significant in the fluorescence line narrowing in ruby. In the experiment of Szabo,[1] however, this was not observed, probably because of insufficient instrumental resolution. Energy transfer and radiation trapping may be negligible for systems with low center concentrations and small absorption coefficients.

We performed experiments on a calcium metaphosphate glass doped with 1 mol% of Eu^{3+} ions. A glassy host was chosen for the reason of large inhomogeneity of the crystal field. From the low Eu^{3+} concentration, large strain broadening and small oscillator strength of the transition, the spectral diffusion is considered to be negligibly small in this system. This is supported by the studies of energy migration among Eu^{3+} ions in this material made by Motegi and Shionoya[4] with samples containing a much higher Eu^{3+} concentration. Figure 1 shows the arrangement of the experimental apparatus employed in our measurement. The excitation source was a cw dye laser (Spectra Physics model 370) with rhodamine 6G pumped by an Ar^+-ion laser. Two glass plates of 1.4 mm thickness were inserted in the dye-laser cavity to obtain frequency tunable output of a single spectral line with the full width at half-maximum (FWHM) of about 0.016 nm (~0.5 cm^{-1}) in the 560–630 nm wavelength range. The $^7F_{0,1,2}$-$^5D_0$ transition energies of Eu^{3+} lie within this tunable range (cf. Fig. 2). Using a double chopper rotated by a single motor, measurements were made on fluorescence at various delay times after the cutoff of the exciting beam. By this method, it was also possible to prevent the laser light from entering the spectrometer. The fluorescence was analysed with a 1-m grating spectrometer (Chromatix model CT-103) and detected with an S-20 type photomultiplier (EMI 9558). Then, the signal was processed in a lock-in amplifier (PAR model 121) and recorded.

Under the excitation by a Hg lamp, as shown in Fig. 3(a), three groups of emission bands appear in the 570–630 nm spectral range at room temperature. These emissions correspond to the transitions from the $^5D_0$ state, whose lifetime is ~0.9 msec at 300 K. The $^5D_0$-$^7F_0$ transition, which is slightly allowed via the mixing of other states, has a half-intensity width of about 70 cm^{-1}. The $^5D_0$-$^7F_1$ emission band at ~590 nm consists of three Stark-split lines overlapped with each other, while the five Stark components are not resolved for the $^5D_0$-$^7F_2$ band at ~612 nm. In contrast with the case of crystal hosts, the spectral widths of the above emission lines are not so much reduced when the temperature is lowered. This fact suggests that the breadths of the emission lines in Fig. 3(a) are determined chiefly by the site-to-site variation of the crystal field acting on the Eu^{3+} ions.

Fluorescence spectrum under the dye-laser excitation at 578 nm is shown in Fig. 3(b), where the resonance fluorescence line is extremely narrowed as expected. A high-resolution measurement re-

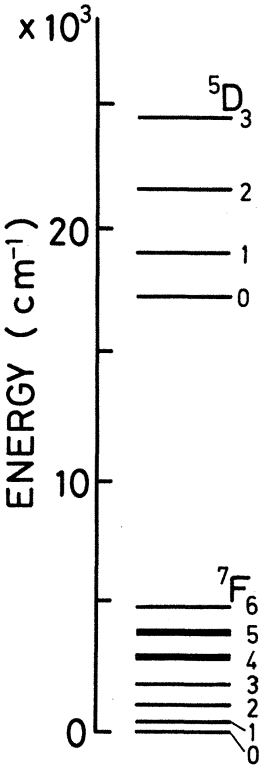

FIG. 2. Energy-level diagram of the Eu^{3+} ion.

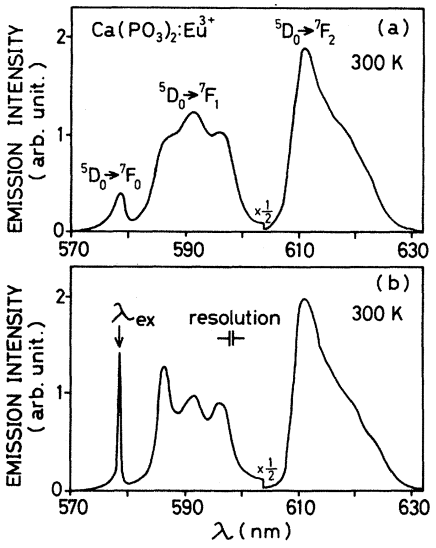

FIG. 3. Emission spectra of $Ca(PO_3)_2 : Eu^{3+}$ (1 mol%) at room temperature: (a) under ultraviolet excitation by a Hg lamp and (b) under monochromatic-light excitation at 578 nm by a cw dye laser. The latter spectrum was measured at 0.6 msec after the excitation.

vealed that the width (FWHM) of this line of 0.20 ± 0.02 nm (6.0 ± 0.6 cm^{-1}) is independent of the exciting laser intensity. Further, by varying the rotational speed of the double chopper, this width was found to be constant between 0.6 and 2 msec after the excitation. Therefore, the spectral diffusion is negligible in our case, and we conclude that the above linewidth is determined solely by homogeneous broadening mechanisms. As shown in Fig. 4, the spectral shape of the narrowed resonance line is described quite well by a Lorentzian. Thus, the homogeneous width (FWHM) of this transition at room temperature is obtained as 3 cm^{-1}, which corresponds to the transverse relaxation time T_2 of ~3.5 psec.[10] This width is very narrow, for example, compared with the typical linewidths of Nd^{3+} ions in various host crystals at room temperature.[11] This fact implies that the $^7F_0$ and $^5D_0$ levels of Eu^{3+} are coupled very weakly with this amorphous host lattice.

Measurements of the luminescence spectra were also made at room temperature under the monochromatic-light excitation in the $^7F_1$-$^5D_0$ and $^7F_2$-$^5D_0$ absorption bands. In this case, a marked narrowing of the resonance fluorescence line was observed only when the excitation was made in the highest-energy region in each band. This result indicates that only the lowest-Stark levels have narrow homogeneous widths at room temperature in the $^7F_1$ and $^7F_2$ manifolds. The widths of the narrowed resonance lines measured are 44 cm^{-1} at 587.5 nm and 25 cm^{-1} at 609 nm. As for the nonresonant emissions in Fig. 3(b), appreciable narrowing is observed only for the 587.5-nm line. If this linewidth (~70 cm^{-1}) results from homogeneous broadening, it should be the average of the widths of the resonance fluorescence lines at 578 and 587.5 nm. Because this is not the case, it is concluded that the contribution of the inhomogeneous broadening mechanism is not negligible in the case of the nonresonant 587.5-nm line of Fig. 3(b). This result means that two ions with the same $^7F_0$-$^5D_0$ energy separation can have different energies between the $^5D_0$ and the lowest-Stark level ϵ_0 of the $^7F_1$ manifold. This cannot be explained unless we take into account the fluctuations of two or more crystal-field components.

When the temperature was lowered, the widths of all the resonance lines measured under the dye-laser excitation decreased. At 77 K, the spectrum of the $^5D_0$-$^7F_0$ fluorescence line was almost the same as that of the exciting light, while the width of the 587.5-nm line was much broader than that of the laser light. This low-temperature emission linewidth of ~5 cm^{-1} is ascribed to the $\epsilon_0 \rightarrow {}^7F_0$ one-phonon relaxation. That the inverse $^7F_0 \rightarrow \epsilon_0$ transition, in addition to the two-phonon Raman scattering, takes part in the broadening of the $^7F_0$ state was verified by analysing the temperature dependence of the resonance linewidth at 578 nm between 270 and 430 K. The observed Lorentzian profile of the resonance fluorescence line is consistent with these relaxation mechanisms, since the ϵ_0-$^7F_0$ energy separation is much larger than the linewidth.[8]

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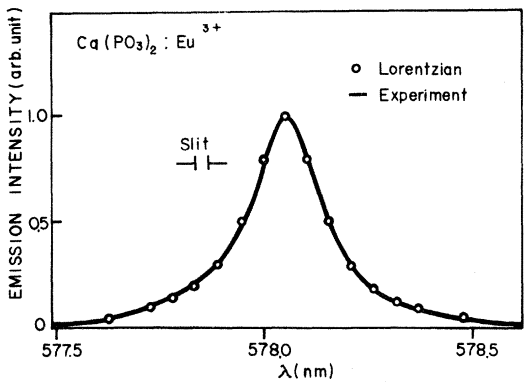

FIG. 4. Spectral shape of the narrowed resonance fluorescence line at 578 nm against the normalized Lorentzian shape.

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