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Radiative and nonradiative relaxation measurements in Ce^{3+} doped crystals*

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Radiative and nonradiative transition rates from the lowest excited Ce^{3+} 5d level in a series of cerium doped oxide and fluoride crystals (Ce^{3+}:LaF_3, Ce^{3+}:CaF_2, Ce^{3+}:$YLiF_4$, Ce^{3+}:$Y_3Al_5O_{12}$, and Ce^{3+}:$YAlO_3$) have been determined by measuring the Ce^{3+} 5d → 4f fluorescence lifetime as a function of sample temperature. The onset of the thermally induced nonradiative transitions occurs for temperatures T^* between 300 and 900 K depending on the host crystal. At temperatures lower than T^*, there is an additional but much weaker temperature dependance of the radiative lifetime. Analysis of the radiative lifetime shows that the radial integral $\langle 4f|r|5d \rangle$ varies by about 20% from the mean value of 0.30 Å among the set of five host crystals, and is a factor of about 1.5 smaller than the free-ion value.

The investigation of radiative and nonradiative relaxation processes from the excited states of impurity doped solids has been and continues to be an active area of research. This activity is driven by both the fundamental interest in ion-lattice interactions as well as the importance of these processes in device applications. Radiative and nonradiative transition rates have been investigated intensively for transition metal ions, color centers, and for the 4f → 4f transitions of rare earth ions in solids. We extend the scope of this work to include the 5d → 4f transition of Ce^{3+} in crystalline solids.

The 4f ↔ 5d transitions of cerium doped crystals are parity-allowed electric dipole transitions and thus have larger oscillator strengths and shorter radiative lifetimes than the more familiar 4f ↔ 4f transitions of the rare-earth ions. The large Stokes shift ($\sim$1800-5500 cm^{-1}) of these 4f ↔ 5d transitions is indicative of the large change in the ion-lattice coupling due to the larger radial extent of the 5d wave function compared to the 4f wave function as well as the lask of shielding of the 5d wave function. Typically, the 4f ↔ 5d transitions of Ce^{3+} lie in the near ultraviolet with transitions energies $\sim$30 000 cm^{-1}.

The 5d → 4f fluorescence transitions of cerium doped crystals are generally thought to have a quantum efficiency near unity at room temperature. However, at temperatures somewhat higher than ambient, nonradiative processes which depopulate the 5d level can become competitive with the radiative process and thus reduce the fluorescence lifetime. In order to study the decay processes of excited cerium ions, we have measured the lifetime of the 5d → 4f fluorescence in a series of Ce^{3+} doped crystals as a function of sample temperature in the interval 12-1200 K. The crystals investigated were Ce^{3+}:LaF_3, Ce^{3+}:CaF_2, Ce^{3+}:$YLiF_4$, Ce^{3+}:$Y_3Al_5O_{12}$, and Ce^{3+}:$YAlO_3$. The samples were mounted either in a cold-finger dewar, or inside a high temperature vacuum furnace. The fluorescence lifetimes were determined by monitoring the lowest 5d → 4f cerium emission intensity following excitation by a frequency-doubled pulsed dye laser as illustrated in fig. 1. The excitation wavelengths were on the long wavelength side of the lowest 5d absorption band in order to prevent any complications arising from photoionization of the cerium ion. Lifetimes as short as 10 ns could reliably be measured without deconvolution of the system response function.

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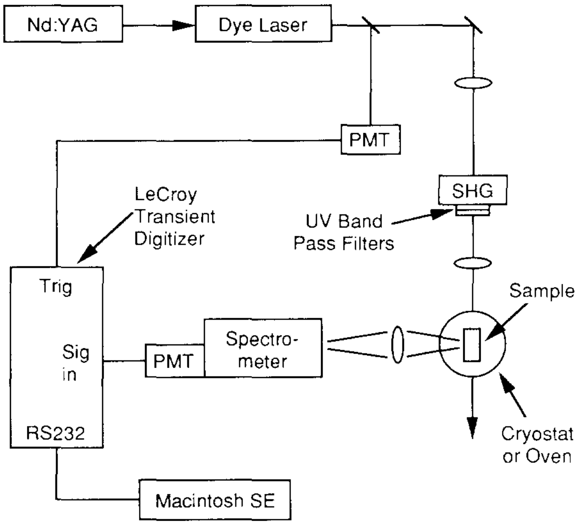

Fig. 1. Experimental apparatus for determining the fluorescence lifetime of Ce^{3+} doped crystals at various temperatures.

Radiative trapping, which could become a problem at higher temperatures due to overlapping emission and absorption profiles, was minimized by careful attention to sample size and cerium concentration.

A graph showing the decay dynamics of the 5d → 4f fluorescence of Ce^{3+}:CaF_2 at two different temperatures is displayed in fig. 2. The decay curves are seen to have an exponential time dependence over two decades at 300 K, where radiative processes dominate, and at 620 K, where the shortening of the lifetime due to the nonradiative relaxation is evident. Exponential decays were observed for all samples and temperatures.

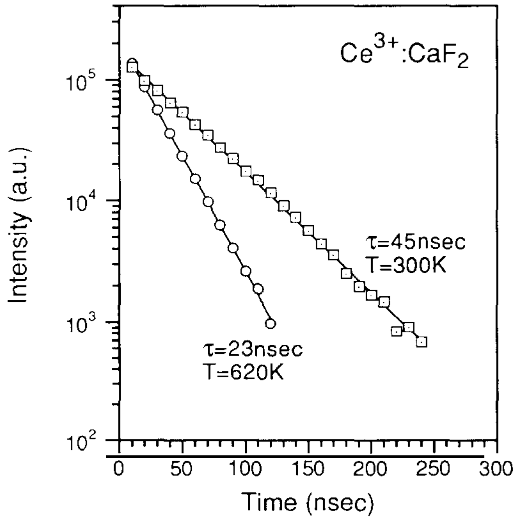

Fig. 2. Decay curves for the fluorescence of the C_{3v} Ce^{3+} ions at 400 nm in Ce^{3+}:CaF_2. The excitation wavelength was 336 nm.

The temperature dependence of the measured fluorescence lifetimes τ for the set of Ce^{3+} doped crystals studied is plotted in fig. 3. The measured lifetime values for Ce^{3+}:$Y_3Al_5O_{12}$ agree with those previously determined by Weber [1]. The measurements in Ce^{3+}:$YLiF_4$, were limited to temperatures less than 1000 K due to sample melting at ~1100 K. The Ce^{3+}:CaF_2 sample undergoes a partial conversion of cerium C_{4v} sites to C_{3v} sites after thermal cycling in the vacuum oven. The data presented in fig. 3 for Ce^{3+}:CaF_2 is that of the C_{3v} sites.

The total decay rate is given by

$$\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}, \tag{1}$$

where τ is the measured fluorescence lifetime of the 5d → 4f transition and τ_r and τ_{nr} are the contributions from radiative and nonradiative processes, respectively. Two distinct trends are evident in the data for each host. Radiative transitions dominate at the lower temperatures where a slow increase of τ_r with increasing temperature is apparent. The rapid decrease of τ at higher temperatures is well correlated with diminishing fluorescence intensity and is attributed to the onset of nonradiative transitions. The nonradiative decay rates W_{nr} are calculated from

$$W_{nr} = \tau^{-1} - \tau_r^{-1}, \tag{2}$$

where $\tau_r = \tau_0 \exp(\alpha T)$. The expression for τ_r is strictly empirical and provides a convenient form to extrapolate the nonradiative rates at higher temperatures. Figure 3 illustrates the temperature variation of the nonradiative rate for Ce^{3+}:$Y_3Al_5O_{12}$, which has been fit assuming that the functional form of W_{nr} is the Arrhenius equation,

$$W_{nr} = s \exp(-\Delta E/kT). \tag{3}$$

The value of ΔE = 6500 cm^{-1} is close to but smaller than the 10 000 cm^{-1} energy gap between the lowest 5d level of Ce^{3+} and the conduction band edge of $Y_3Al_5O_{12}$ [2]. We have thus attributed the nonradiative relaxation to a thermally induced

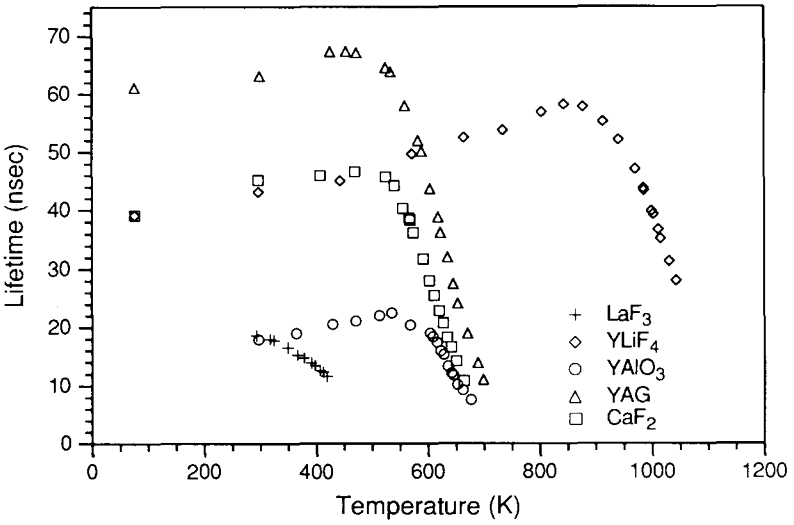

Fig. 3. Measured fluorescence lifetimes for the set of Ce^{3+} doped crystals as a function of sample temperature.

ionization of the 5d electron into conduction band. Such a process has been previously used to explain the nonradiative relaxation in Sm^{2+} doped fluoride crystals [3] and for F centers in alkali halide crystals [4]. High temperature photoconductivity measurements are required to confirm this model. The fit parameters for the nonradiative decay process in the set of cerium doped crystals is summarized in table 1.

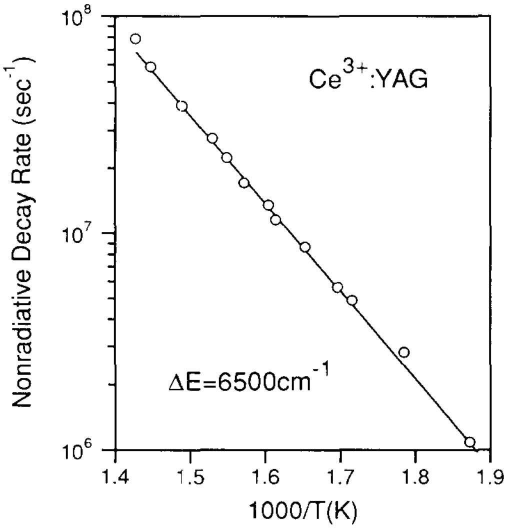

Fig. 4. Nonradiative decay rate for Ce^{3+}:Y$_3$Al$_5$O$_{12}$ as a function of inverse temperature. The activation energy ΔE is 6500 cm^{-1}.

The radiative lifetime can be written as

$$\frac{1}{\tau_r}=\frac{64\pi^4 e^2\chi}{3hg_i\lambda^3}\sum_f S_{if}, \tag{4}$$

where the sum extends over all the states in the 4f manifold, S_{ij} is the electric dipole line strength, λ is the peak emission wavelength, and $\chi \approx n(n^2+2)^2/9$ is a correction term due to the index of refraction n of the host. The temperature variation in the index of refraction due to thermal expansion is too small to account for the observed variation in τ_r. A more probable explanation is the mixing of opposite parity states into either the 4f or 5d levels. Such a process would steal oscillator

Table 1

Summary of the nonradiative decay parameters for the set of Ce^{3+} doped crystals, where E is the approximate no-phonon energy of the lowest 5d→4f($^2F_{5/2}$) transition, s and ΔE are the fitting constants for the Arrhenius function, and T^* is the roll-off temperature at which the nonradiative rate becomes comparable to the radiative rate.

Sample	E (cm^{-1})	s (s^{-1})	ΔE (cm^{-1})	T^* (K)
Ce:LaF$_3$	37 700	1×10^{11}	2 400	310
Ce:YAG	20 400	4×10^{13}	6 500	500
Ce:CaF$_2$	29 100	1×10^{14}	6 700	540
Ce:YAlO$_3$	30 800	1×10^{17}	9 700	590
Ce:YLiF$_4$	33 000	4×10^{15}	14 000	920

strength from the transition and increase the radiative lifetime. This could include the mixing of the 4f and 5d levels among themselves. Static crystal field mixing of these states is known to be involved in the 4f→4f one-photon and 4f→5d two-photon electric dipole transitions [5] and could be temperature dependent. There is also the thermally induced mixing of the 5d state with the 5p level of the cerium ion or with opposite parity conduction band states. The temperature dependance of the radiative lifetime would depend on the details of the phonon participation in the mixing process.

There is a wide variation in the fluorescence wavelengths, indices of refraction, and radiative lifetimes among the different host crystals used in this study. The expression for the transition rate in eq. (4) can be used to evaluate the relations between these parameters. Hoshina [6] has calculated the line strengths for the $5d(t_{2g}) \rightarrow 4f$ and $5d(e_g) \rightarrow 4f$ transitions for Ce^{3+} in the cubic or octahedral crystal field in terms of the radial integral ⟨4f|r|5d⟩. Using his results in eq. (4), we have estimated the value of ⟨4f|r|5d⟩ for the set of Ce^{3+} doped crystals as shown in table 2. The mean value of ⟨4f|r|5d⟩ is 0.30 Å which is about 1.5 times smaller than the Ce^{3+} free-ion value of 0.45 Å calculated by us, 0.441 Å calculated by Williams et al. [7] or 0.438 Å extrapolated by Judd [8]. This reduction in ⟨4f|r|5d⟩ has been discussed by Krupke [9] in terms of an expansion of the 5d wave function relative to the 4f wave function when the ion is embedded in the lattice. Williams et al. [7] have also noted this reduction with respect to electronic Raman scattering in Ce^{3+} doped $LuPO_4$. However, we do not observe the large (~2×) variation in ⟨4f|r|5d⟩ with host crystal as suggested by Powell et al. [10] or by Chase and Payne [11] for Nd^{3+} ions or in the 4f→5d Ce^{3+} oscillator strength as discussed by Williams et al. [7]. Although we have assumed that the contribution of the angular integrals to the transition moment is independent of the Ce^{3+} coordination, we do not feel that this assumption would significantly mask any variations in the radial integral. Moreover, it should be noted that our determination of the radial integral involves the lowest 5d level and a summation over the 4f levels whereas the other results noted above involve the lowest 4f level and a summation on the 5d states. The nature of the reduction in ⟨4f|r|5d⟩ for the different rare-earth ions is surely a matter for continued investigation.

Table 2
Summary of the radiative decay parameters for the set of Ce^{3+} doped crystals, where τ_r is the extrapolated radiative lifetime at $T=0$ K, λ is the approximate peak emission wavelength, and n is the index of refraction.

Sample	τ_r (ns)	λ (Å)	n	⟨4f|r|5d⟩ (Å)
$Ce:LaF_3$	19.0	2920	1.60	0.29
Ce:YAG	59.1	5500	1.90	0.31
$Ce:CaF_2$	39.0	3700	1.43	0.34
$Ce:YAlO_3$	17.1	3620	1.98	0.28
$Ce:YLiF_4$	35.7	3200	1.49	0.27

References

[1] M.J. Weber, Solid State Commun. 12 (1973) 741.
[2] D.S. Hamilton, S.K. Gayen, G.J. Pogatshnik, R.D. Ghen and W.J. Miniscalco, Phys. Rev. B 39 (1989) 8807.
[3] L.L. Chase, Stephen A. Payne and Gary D. Wilke, J. Phys. C 20 (1987) 953.
[4] W. Beal Fowler, in: Physics of Color Centers, ed. W. Beal Fowler (Academic, New York, 1968) p. 97.
[5] S.K. Gayen, D.S. Hamilton and R.H. Bartram, Phys. Rev. B 34 (1986) 7517.
[6] Teruhiko Hoshina, J. Phys. Soc. Jpn. 45 (1980) 1261.
[7] G.M. Williams, N. Edelstein, L.A. Boatner and M.M. Abraham, Phys. Rev. B. 40 (1989) 4143.
[8] B.R. Judd, Inor. Chim. Acta 139 (1987) 341.
[9] William F. Krupke, Phys. Rev. 145 (1966) 325.
[10] R.C. Powell, S.A. Payne, L.L. Chase and G.D. Wilke, Phys. Rev. B 41 (1990) 8593.
[11] L.L. Chase and S.A. Payne, Phys. Rev. B 34 (1986) 8883.