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The unusual temperature dependence of the Eu^{2+} fluorescence lifetime in CaF_2 crystals

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Abstract

Fluorescence lifetimes of Eu^{2+} doped in CaF_2 are measured at various temperatures between 4 and 450 K. The lifetime increases between 100 and 320 K, in contrast to the usual lifetime–temperature dependence. At higher or lower temperatures, the lifetime decreases with increasing temperature. This phenomenon is explained by simulation of the energy levels and lifetimes of low-lying $4f^65d$ states involved in the fluorescence.

Keywords: Fluorescene lifetime; Europium; CaF_2

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1. Introduction

The $4f^N \rightarrow 4f^{N-1}5d$ absorption and $4f^{N-1}5d \rightarrow 4f^N$ emission spectra of lanthanide ions in crystals are usually characterized by multi-phonon broad bands as a consequence of the large difference in the strength of interactions with ligands between 4f and 5d orbitals. In most cases, the lifetimes of excited states decrease with increasing temperature as a result of a substantial increase in non-radiative relaxation rate (the radiative relaxation rate usually also increases slightly). In contrast, for Eu^{2+} in CaF_2 [1–3] and some other crystals [4,5] the lifetime of the excited state increases with increasing temperature from about 10 K to room temperature. So far only qualitative explanations have been given for this phenomenon.

In this work, we carry out systematic measurements of excited state lifetimes of Eu^{2+} doped in CaF_2 at various temperatures from 4 to 450 K to clarify the experimental results and then calculate the energy level structure and lifetime of the $4f^65d$ excited configuration to simulate the measured results.

2. Experimental results

Laser excitation was provided by a small nitrogen pulsed laser. Pulse duration and energy were approximately 2 ns and 100 μJ, respectively. The powdered $CaF_2 : 0.1$ mol% Eu sample was mounted in an Oxford Microstat cold finger liquid helium cryostat. Sample temperatures could be varied from 5 to 500 K using a resistive heater attached to the cold finger.

The emission from the sample was collected by quartz optics and detected in two separate systems for fluorescent lifetime or spectral measurement. A 10 cm Bausch and Lomb monochromator equipped with an EMI 9659 photomultiplier tube tuned to the peak of the f–d emission was used for the lifetime measurements. The PMT signal was averaged on a digital oscilloscope and downloaded to a computer for processing.

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For spectral measurements, the emission was collected by a quartz fibre optic bundle and analyzed by a TRIAX 320 spectrograph, equipped with a liquid nitrogen cooled CCD. Measurements of the lifetime and f–d emission spectrum were recorded at various sample temperatures.

At low temperature (lower than 50 K), the emission spectra are characterized by sharp zero-phonon line at around 413 nm companied by a broad vibronic band centered at 425 nm with some one-phonon lines clearly distinguishable. These one-phonon lines and zero-phonon line become indistinguishable around 80 and 120 K, respectively. The vibronic band becomes broader as temperature increases.

The decay curves were all found to be exponential with time so each curve gives a single lifetime for a certain temperature. The lifetime did not vary across the emission band. The results are listed in Table 1. It can be seen that between 100 and 320 K, the lifetime increases with increasing temperature, which is similar to early findings [2]. However, at temperatures lower than 100 K, the measured lifetime shows the usual trend of decreasing with increasing temperature, different from Ref. [2]. At higher temperatures, the lifetimes show the usual trend of rapid decrease with increasing temperature, which we attribute to a large increase in the nonradiative relaxation rate.

Table 1
The lifetime of Eu^{2+}:CaF_2 measured at different temperatures

T (K)	τ(ns)
10.8	671
21.2	666
33.6	657
46.3	660
60.1	658
77.1	652
95.2	653
110	649
125	654
145	663
165	668
205	683
225	690
245	697
265	705
285	716
295	716
300	714
305	717
315	716
325	704
335	681
345	652
355	604
365	543
375	467
385	386
395	307
405	231
415	175
435	93
445	77
455	57
465	42

T, temperature; $\tau(T)$, lifetime at T.

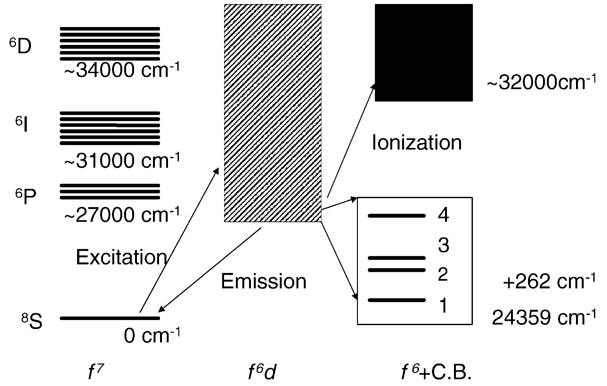

Fig. 1. Schematic diagram of the energy level structure and dynamical processes for Eu^{2+}:CaF_2. The ground state is comprised of three nearly degenerate energy levels of $^8S_{7/2}$ of $4f^7$ (the total degeneracy is 8). The energy levels of the excited configuration $4f^65d$ form a quasi-continuous band starting from around 24,000 cm^{-1}. The conduction band due to ionization of 5d electron to conduction band starts at an energy around 32,000 cm^{-1}. The lowest excited multiplets of $4f^7$ are at around 27,000, 31,000 and 34,500 cm^{-1}. The excitation forms a thermal equilibrium distribution among the lowest excited $4f^65d$ energy levels due to fast non-radiative relaxation among them. These states either relax to the ground states by emitting a photon or ionize to the conduction band.

3. Theoretical simulation and discussion

The dynamical processes of excitation in Eu^{2+}:CaF_2 are shown in Fig. 1. The lowest excited states belong to the $4f^65d$ configuration. The excitation to $4f^65d$ bands quickly relax to the bottom of the band and than relax radiatively to the ground states of $4f^7$ configuration by emitting a photon or nonradiatively by either a multi-phonon processes or by ionization of the 5d electron to conduction band [6,7].

Methods for simulating one-photon and two-photon absorption spectra of Eu^{2+} in CaF_2 have been developed using an extended crystal-field Hamiltonian [8–11] which takes into account major interactions in both $4f^N$ and $4f^{N-1}5d$ configurations and the interaction between them [12]. The simulations have successfully explained energy level positions, one-photon and two-photon transition intensities and line widths [12].

There are around 30,000 states in $4f^65d$ configuration. The lowest few hundred of them in the range of 24,000–30,000 cm^{-1} are spin octet states and have a large line strength for transitions from and to the near-degenerate ground octet multiplet $^8S_{7/2}$ of $4f^7$ configuration [6]. Because of fast nonradiative relaxation among these $4f^65d$ states, there is thermal equilibrium among these $4f^65d$ excited states before fluorescence occurs. This explains why the fluorescence lifetime does not vary across the emission band. Radiative relaxation from each of these excited states gives a broad band, with zero-phonon and some one-phonon lines distinguishable at only low temperatures. A superposition

Table 2
Calculated energy levels, their relative radiative relaxation rates and degeneracies, where i, g_i, E_i, ΔE_i and R_i are energy level no., degeneracy, energies, energies relative to the first energy level and relative relaxation rate, respectively

i	g_i	E_i	ΔE_i	R_i
1	4	24359	0	1.000
2	4	24621	262	0.128
3	2	24668	309	1.528
4	2	25007	648	0.496
5	4	25046	687	0.472
6	2	25387	1028	1.043

The units of E_i and ΔE_i are cm^{-1}. Only the lowest few energy levels contribute to the lifetime. *Note*: The absolute relaxation rate is proportional to the square of the effective radial integral $\langle f|r|d\rangle$, which cannot be calculated accurately. It is treated as an adjustable parameters in this work.

of the transitions allows us to calculate the emission spectrum and lifetime as a function of temperature. The lowest few $4f^65d$ energy levels, their degeneracy, and relative radiative relaxation rates are presented in Table 2. The relaxation rate of the thermal-equilibrium states can be written as:

$$R_R = \frac{1}{\tau_1}\frac{\sum_i g_i R_i\ \exp(-\Delta E_i/kT)}{\sum_i g_i\ \exp(-\Delta E_i/kT)}. \tag{1}$$

In this expression, τ_1 is the lifetime at 0 K, g_i the degeneracy of the state, R_i the relative radiative decay rate, ΔE_i the energy difference between the ith state and the lowest excited state, k the Boltzmann's constant, and T is the temperature.

The dramatic decrease of lifetimes with increasing temperature above room temperature is common in fluorescence materials. It is usually due to a rapid increase in nonradiative relaxation rate. As the temperature increases, both the nonradiative multiphonon relaxation rate [13] and the nonradiative relaxation of excitation due to ionization of 5d electron to conduction band [7] increase sharply at high temperature. Phenomenologically, the nonradiative relaxation rate R_{NR} can be written as:

$$R_{NR} = W_{NR}\ \exp\left(\frac{-E_i}{kT}\right), \tag{2}$$

where the non-radiative rate constant W_{NR} and the activation energy E_i are treated as parameters. This mechanism only contributes significantly at room temperature or even higher temperature.

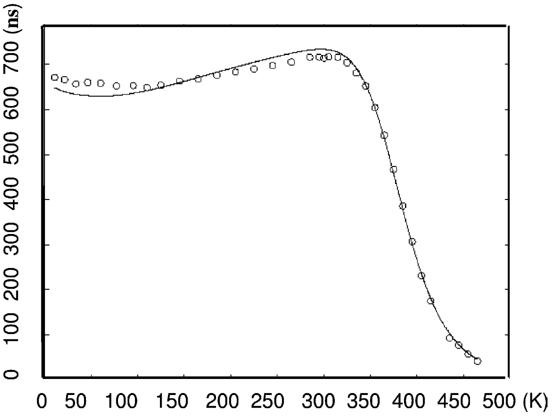

Fig. 2. Measured and calculated lifetimes as a function of temperature. Measured lifetimes are shown as circles. The calculated lifetimes are shown as a curve. The values of parameters are obtained by least square fitting as $\tau_1 = 644$ ns, $A = -0.05$, $E_A = 20\,\text{cm}^{-1}$, $W_{NR} = 1.23 \times 10^{14}\,\text{s}^{-1}$ and $E_i = 4370\,\text{cm}^{-1}$.

The electronic energy levels also couple with vibrations. At zeroth order approximation, the electronic and vibrational states can be considered as two independent systems and the lifetime of the states of the electron–phonon (EP) system is independent of the vibronic states. However, for higher-order approximations, especially when the electronic states and the vibrational modes are degenerate, the coupled EP states split into several states, the first few of which separate from each other by a few to a hundred wavenumbers [14]. These coupled EP states can have slightly different radiative relaxation rates. This effect may be modeled phenomenologically as follows:

$$\Delta R = \frac{1}{\tau_1} A\left[1 - \exp\left(\frac{-\Delta E_A}{kT}\right)\right], \tag{3}$$

where, again, A and E_A are treated as fitting parameters. This mechanism contributes significantly only at low temperature.

The lifetime at any temperature can be calculated by combining the above rates to give:

$$\tau(T) = \frac{1}{R_R(T) + \Delta R(T) + R_{NR}(T)} \tag{4}$$

with five fitting parameters τ_1, W_{NR}, E_i, A and E_A.

The experimental results and the fitted results are plotted in Fig. 2. The parameter values used are listed in the figure caption. It can be seen that the calculated curve gives the right trend of lifetime as a function of temperature. However, the calculated lifetime increase is greater than the measured lifetime. A possible explanation is that the radiative transition rate of each state increases due to a deviation from the Condon approximation.

4. Conclusion

The fluorescence lifetime of the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} doped in CaF_2 has been measured at various temperatures between 4 and 450 K. Between 100 and 320 K, the lifetime increases with increasing temperature, different from the usual lifetime–temperature dependence. Energy levels of $4f^7$ and $4f^65d$ configurations and transitions rates between them have been calculated using an extended crystal-field Hamiltonian. The results show that several excited $4f^65d$ energy levels separated by energies of a few hundred wavenumbers contribute to the excited state lifetimes. The lowest excited state has a much larger radiative decay rate than the other excited states that are thermally populated. As temperature increases, the chance of initial states occupying higher excited energy levels, which have a smaller radiative decay rate, increases and therefore the average radiative decay rate decreases. Between 100 and 320 K in CaF_2, the radiative decay dominates the 5d → 4f excitation relaxation and therefore we observe an increasing lifetime with increasing temperature. At low or high temperatures, the lifetime decreases with increasing temperature due to thermal activation and quenching effects.

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References

[1] P. Kisliuk, H.H. Tippins, C.A. Moore, S.A. Pollack, Phys. Rev. 171 (1968) 336.
[2] T. Tsuboi, P. Silfsten, J. Phys.: Condens. Matter 3 (1991) 9163.
[3] S.H. Poort, A. Meijerink, G. Blasse, J. Phys. Chem. Solids 58 (1997) 1451.
[4] J.P. Spoonhower, M.S. Burberry, J. Lumin. 43 (1989) 221.
[5] A. Meijerink, G. Blasse, J. Lumin. 47 (1990) 1.
[6] C. Dujardin, B. Moine, C. Pedrini, J. Lumin. 54 (1993) 259.
[7] C. Dujardin, B. Moine, C. Pedrini, J. Lumin. 38 (1987) 193.
[8] M.F. Reid, L. van Pieterson, R.T. Wegh, A. Meijerink, Phys. Rev. B 62 (2000) 1291.
[9] L. van Pieterson, M.F. Reid, R.T. Wegh, S. Soverna, A. Meijerink, Phys. Rev. B 65 (2002) 045113.
[10] L. van Pieterson, M.F. Reid, G.W. Burdick, A. Meijerink, Phys. Rev. B 65 (2002) 045114.
[11] M.F. Reid, L. van Pieterson, A. Meijerink, J. Alloys Compd. 344 (2002) 240.
[12] G.W. Burdick, A. Burdick, V. Deev, C.K. Duan, M.F. Reid, Unpublished data, 2003.
[13] M. Sturge, Phys. Rev. B 8 (1973) 6.
[14] L.L. Chase, Phys. Rev. B 2 (1970) 2308.