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Phonon annihilation and excited-state absorption processes in Sm^{2+}:BaClF

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Using selective pulsed laser excitation into the first metastable excited state $^5D_0$ of the Sm^{2+}:BaClF system, we have observed an anti-Stokes fluorescence originating from the $^5D_1$ multiplet located at 1339 cm^{-1} above $^5D_0$ at temperatures ranging from 295 to 650 K. At long times after the laser pulse, the $^5D_1$ and $^5D_0$ fluorescences decay exponentially with the same time constant. At shorter times, the $^5D_1$ emission exhibits either an initial rise or a fast decay depending on the laser beam intensity, the $^5D_0$ fluorescence decay remaining purely exponential in any case. Under the same excitation conditions but at low temperature, we have also observed the anti-Stokes fluorescence from the $^5D_2$ multiplet located at 3280 cm^{-1} above the $^5D_0$ pumping state, in addition to that originating from $^5D_1$. These new experiments give direct evidence of phonon annihilation and excited-state absorption processes in the Sm^{2+}:BaClF system.

I. INTRODUCTION

Evidence of phonon annihilation processes in the excited states of the Sm^{2+}:BaClF system was first reported by Alam and di Bartolo.[1,2] This assertion was supported by the fact that at temperatures above 280 K the decay curve of the fluorescence originating from the $^5D_1$ multiplet (15 872 cm^{-1}) was observed to include a long tail with a time constant equal to the lifetime of the $^5D_0$ state lying 1339 cm^{-1} lower down. This observation was corroborated by cw fluorescence measurements which showed that the $^5D_1$ fluorescence intensity increased relative to the $^5D_0$ one, according to a Boltzmann law, as the temperature was raised from 400 to 600 K. These experiments (it is important to point it out) were performed with the use of flash tubes or lamps, providing an optical excitation in the ultraviolet region. Under these experimental conditions the Sm^{2+}:BaClF system is excited into $4f^5$-$5d$ states which are connected both to $^5D_1$ and $^5D_0$ by fast nonradiative transitions, ensuring the feeding of these two metastable levels.

More recently, we performed investigations in the relaxation mechanisms of the Sm^{2+} centers in BaClF, using selective excitation into the $^5D_1$ level.[3–6] We focused our attention on the (1.6—300)-K thermal range. The decay patterns of the $^5D_1$ fluorescence were observed to be purely exponential and no long tail was appearing, as is the case under uv excitation. We also pumped the system into the $^5D_2$ level located at 1941 cm^{-1} above $^5D_1$.[4,5] All the data gained with the use of selective excitation either in the $^5D_1$ or in the $^5D_2$ multiplet were found to be consistent with the assumption that the $^5D_0 \rightarrow {}^5D_1$ upward nonradiative transition is negligible at temperatures as high as 300 K. This appeared to be in contradiction with the observations reported by Alam and di Bartolo.

Removing this point of controversy required a selective excitation of the system into the $^5D_0$ state with intentions of looking at the possible $^5D_1$ fluorescence resulting from the pumping by phonon annihilation in the $^5D_1$ multiplet from the $^5D_0$ lower level. We report in the present paper the results of this experiment. Section II is concerned with the underlying theoretical background. The experimental results are presented and discussed in Sec. III.

II. THEORETICAL CONSIDERATIONS

Let us assume that the Sm^{2+}:BaClF system is optically pumped into the lowest excited state $^5D_0$ with pulsed selective excitation at a temperature T near or above room temperature. Under these conditions, the system may be seen as a multilevel system with two metastable fluorescent levels $^5D_0$ and $^5D_1$ (Fig. 1). The response to pulsed excitation of such a system has been thoroughly treated.[7] Let τ_0 and τ_1 be the respective lifetimes of levels $^5D_0$ and $^5D_1$ on one hand, and P_{10} and P_{01} the rates of the

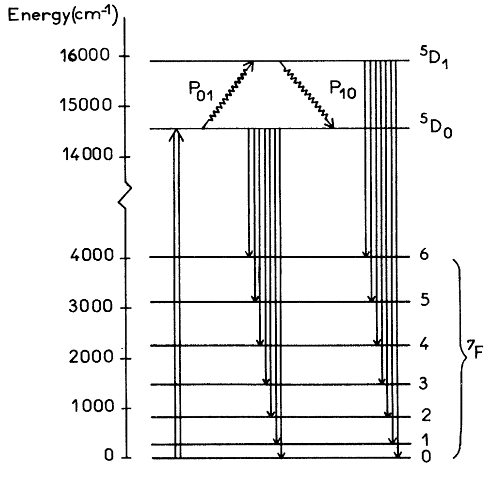

FIG. 1. Deexcitation scheme of the Sm^{2+}:BaClF system under selective excitation into the $^5D_0$ state at room temperature.

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$^5D_1 \rightarrow {}^5D_0$ downward and $^5D_0 \rightarrow {}^5D_1$ upward radiationless transitions, on the other hand. Since intraconfigurational f-f radiationless transitions in lanthanides provide typical examples of the weak-coupling limit, the relation between P_{10} and P_{01} is well described by[8]

$$P_{01}(T)=P_{10}(T)\exp\left[-\frac{\Delta E_{10}}{kT}\right], \qquad (1)$$

where ΔE_{10} is the $^5D_1 - {}^5D_0$ energy gap (1339 cm^{-1}). Near room temperature, τ_0, τ_1, and P_{10} were found to fall in the region of 1.6 ms, 160 μs, and 5×10^3 s^{-1}, respectively.[2–6] According to Eq. (1), the rate P_{01} should not exceed 10 s^{-1}. Under these conditions, the respective instantaneous populations $n_0(t)$ and $n_1(t)$ of levels $^5D_0$ and $^5D_1$, for times after the end of the pulse, may be expressed as follows[7]:

$$\begin{aligned} n_0(t) &= (N_0+N_1\alpha_{10})\exp\left[-\frac{t}{\tau_0}\right] \\ &\quad -\alpha_{10}\left[N_1-N_0\frac{P_{01}}{P_{10}}\alpha_{10}\right]\exp\left[-\frac{t}{\tau_1}\right], \\ n_1(t) &= \left[N_1-N_0\frac{P_{01}}{P_{10}}\alpha_{10}\right]\exp\left[-\frac{t}{\tau_1}\right] \\ &\quad +\frac{P_{01}}{P_{10}}\alpha_{10}(N_0+N_1\alpha_{10})\exp\left[-\frac{t}{\tau_0}\right]. \end{aligned} \qquad (2)$$

N_0 and N_1 stand for the respective populations of levels $^5D_0$ and $^5D_1$ at the end of the pulse assumed to be the time origin and $\alpha_{10}=P_{10}(\tau_1^{-1}-\tau_0^{-1})^{-1}$. It is to be pointed out that Eqs. (2) are valid only if the following condition is verified:

$$(\tau_1^{-1}-\tau_0^{-1})^2 \gg 4P_{10}P_{01}\ . \qquad (3)$$

Let us assume finally that the duration $\Delta\tau$ and the period τ of the excitation pulses verify the following relations:

$$\Delta\tau \ll \tau_1, \tau_0 \ll \tau \qquad (4)$$

Then neither radiative nor radiationless deexcitations from levels $^5D_0$ and $^5D_1$ have the chance to occur during each pulse. The population of the $^5D_1$ level remains equal to zero during the pumping of the system, the relaxation of which being completely achieved between two consecutive pulses.

Thus Eqs. (2) reduce to

$$\begin{aligned} n_0(t) &= N_0\left[\exp\left[-\frac{t}{\tau_0}\right]+\frac{P_{01}}{P_{10}}\alpha_{10}^2\exp\left[-\frac{t}{\tau_1}\right]\right] \\ &\approx N_0\exp\left[-\frac{t}{\tau_0}\right], \\ n_1(t) &= N_0\frac{P_{01}}{P_{10}}\alpha_{10}\left[\exp\left[-\frac{t}{\tau_0}\right]-\exp\left[-\frac{t}{\tau_1}\right]\right]. \end{aligned} \qquad (5)$$

Thus, the pulsed laser excitation into the $^5D_0$ level is expected to induce a fluorescence originating from both levels $^5D_0$ and $^5D_1$: The $^5D_0$ emission should appear to decay exponentially with the time constant τ_0, while the $^5D_1$ one should exhibit a rise, followed by an exponential decay with the same time constant τ_0. This should also take place at any temperature at which the conditions (3) and (4) remain valid.

At this point, it is of importance for what comes hereafter to look at the possibility of observing a double decay in the $^5D_1$ decay curve. It is obvious that the initial condition $n_1(0)=N_1=0$ leading to Eqs. (5) definitely prevents this opportunity to occur. On the other hand, if we assume that some process, to be presented later, ensures a nonzero population of the $^5D_1$ level at the end of the pulse, then Eqs. (2) predict a double decay of the $^5D_1$ fluorescence if

$$\frac{N_1}{N_0} > \frac{P_{01}\tau_1}{1+(P_{01}\tau_1/P_{10}\tau_0)\alpha_{10}^2} \approx P_{01}\tau_1\ . \qquad (6)$$

In the opposite case, the $^5D_1$ fluorescence should experience an initial rise before decaying. Thus the $^5D_1$ fluorescence at short times after the pulse depends strongly on the ratio N_1/N_0, i.e., on the efficiency of the process which provides a nonzero initial population of the $^5D_1$ level.

III. EXPERIMENTAL

A. Materials and techniques

The sample used in the present study is a BaClF single crystal doped with 0.5% Sm^{2+}. Temperatures up to 650 K were obtained with the aid of a helium-filled furnace equipped with a copper Constantan thermocouple. Pumping of the system into the $^5D_0$ state was achieved with the use of a frequency-doubled yttrium aluminum garnet (YAG):Nd^{3+} laser (pulse duration 15 ns, repetition rate 10 Hz) followed by a three amplifier stage dye laser (linewidth 0.1 cm^{-1}), ensuring an output energy of about 30 mJ per pulse at the wavelength of the $^7F_0 \rightarrow {}^5D_0$ pumping transition ($\sim$6875 Å at room temperature). The fluorescence data were obtained with the use of conventional techniques described elsewhere.[9]

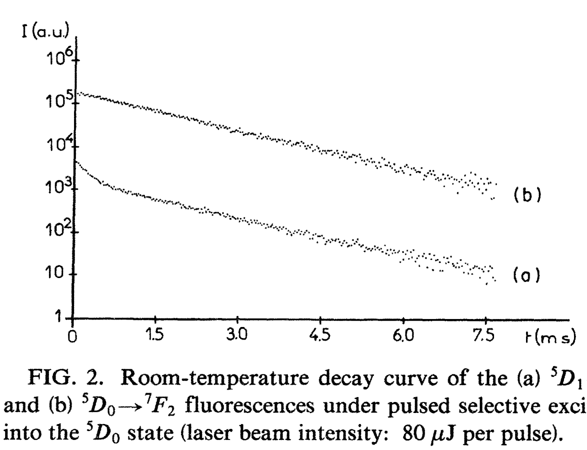

FIG. 2. Room-temperature decay curve of the (a) $^5D_1 \rightarrow {}^7F_1$ and (b) $^5D_0 \rightarrow {}^7F_2$ fluorescences under pulsed selective excitation into the $^5D_0$ state (laser beam intensity: 80 μJ per pulse).

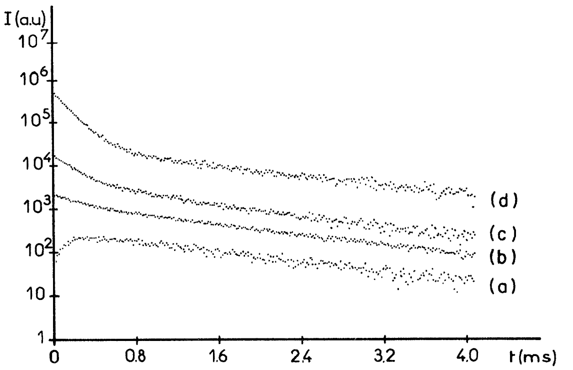

FIG. 3. Room-temperature decay curve of the ${}^5D_1 \rightarrow {}^7F_1$ fluorescence under pulsed selective excitation into the ${}^5D_0$ state at different laser beam intensity levels: (a) 3 μJ, (b) 30 μJ, (c) 100 μJ, and (d) 370 μJ per pulse.

B. Results

To begin with, the sample was pumped at room temperature with a focused beam of intensity about 80 μJ per pulse adjusted at the wavelength of the ${}^7F_0 \rightarrow {}^5D_0$ transition ($\sim$6875 Å). Indeed, a fluorescence originating from both levels ${}^5D_0$ and ${}^5D_1$ was observed. It was verified that both ${}^5D_0$ and ${}^5D_1$ fluorescences have identical excitation spectra in the (687–688)-nm spectral range. The decay curves of the ${}^5D_1 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ emissions are shown Fig. 2. First, it appears that at long times after the pulse both fluorescences decay exponentially with the same time constant ($\sim$1.48 ms) characteristic of the room-temperature ${}^5D_0$ lifetime in this material. This is in agreement with the predictions in Sec. II and confirms the thermalization between levels ${}^5D_0$ and ${}^5D_1$ in this system, as reported in Refs. 1 and 2. On the other hand, the ${}^5D_1$ fluorescence experiences in the (0–1.6)-ms time interval an additional decay with a shorter time constant, nothing like that being visible in the ${}^5D_0$ decay curve. This observation is quite inconsistent with the assumption that the ${}^5D_1$ population at the end of the excitation pulse is equal to zero. Thus a process should take place which provides a feeding of the ${}^5D_1$ multiplet during the pulsed laser excitation into the ${}^5D_0$ state. The possibility of the process under question to originate from some energy transfer between Sm^{2+} ions was ruled out, since no changes appear in the observed phenomena as the Sm^{2+} concentration was lowered from 0.5% to 0.01%. Then, looking at the dependence of the laser beam intensity, it appeared that the initial short decay in the ${}^5D_1$ decay curve is removed by a rise as the beam intensity is reduced, the exponential tail remaining unchanged in any case, as shown in Fig. 3. From the fitting of the ${}^5D_1$ decay curves, it is easy to derive the ratio N_1/N_0 of the respective initial populations of levels ${}^5D_1$ and ${}^5D_0$, taking Eqs. (2) into account:

$$\frac{N_1}{N_0}=\left[1+\frac{A_{11}}{A_{10}}\right]\frac{(P_{01}/P_{10})\alpha_{10}}{1-(1+A_{11}/A_{10})(P_{01}/P_{10})\alpha_{10}^2}\,, \tag{7}$$

where A_{11} and A_{10} are the fitted algebraic amplitudes of the exponential terms with the τ_1 and τ_0 time constants, respectively, in the experimental ${}^5D_1 \rightarrow {}^7F_1$ decay curve. The plot of N_1/N_0 versus the laser beam intensity W is shown in Fig. 4, the relevant quantities τ_0^{-1}, τ_1^{-1}, P_{10}, and P_{01} being taken equal to 680, 6470, 5458, and 8 s^{-1}, respectively, in agreement with the room-temperature data

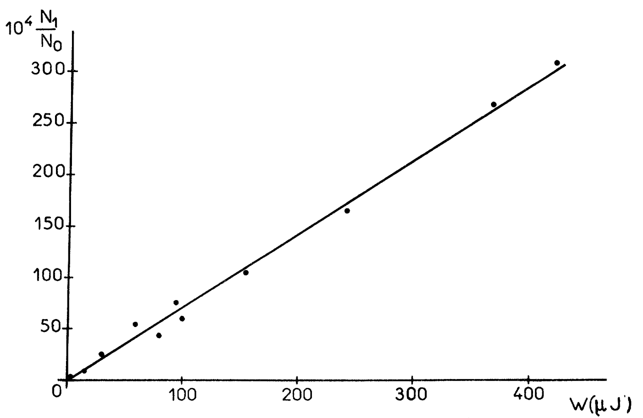

FIG. 4. Dependence of the N_1/N_0 ratio vs the laser beam intensity W (N_1 and N_0 are the respective populations of the ${}^5D_1$ and ${}^5D_0$ levels at the end of the excitation pulse).

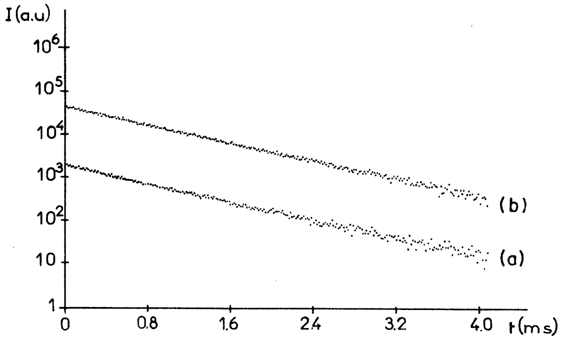

FIG. 5. Decay curve of the (a) ${}^5D_1 \rightarrow {}^7F_1$ and (b) ${}^5D_0 \rightarrow {}^7F_2$ fluorescences under pulsed selective excitation into the ${}^5D_0$ state at 540 K (laser beam intensity: 80 μJ per pulse).

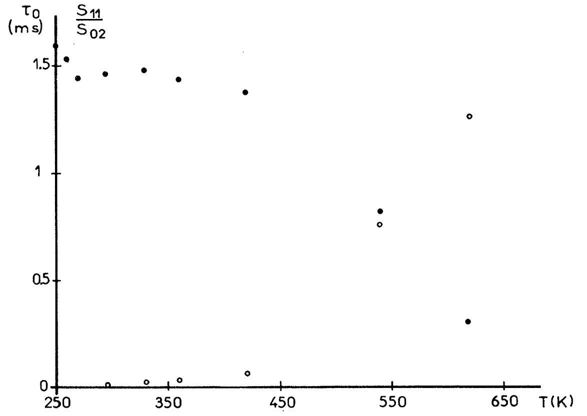

FIG. 6. Temperature dependence between 250 and 650 K of (●) the decay time τ_0 of the ${}^5D_0$ fluorescence, (○) the ratio of the integrated areas S_{11} and S_{02} corresponding, respectively, to the ${}^5D_1 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions under pulsed selective excitation into the ${}^5D_0$ state.

in this work and in previous works.[4–6] N_1/N_0 appears to be proportional to W. Thus N_1 shows a quadratic dependence on the beam intensity since it is reasonable to assume that N_0 is proportional to W. This result is in agreement with the assumption that the "feeding" of the $^5D_1$ level during the excitation pulse originates from a two-photon absorption process. This process presumably involves the $^5D_0$ state as a transition step on the way from the initial to the final state, the second photon promoting the Sm^{2+} ion from the $^5D_0$ excited state up to a $4f^5$-$5d$ state. Indeed, the alternative process, consisting of the simultaneous absorption of two photons promoting the Sm^{2+} ion from the $^7F_0$ ground state up to a $4f^6$ excited state, is much less probable in this system, since the $4f^6 \rightarrow 4f^5$-$5d$ transition involved in the two-step process is electric dipole allowed. Now, it is of interest to point out that as predicted from the condition (6) the threshold value of N_1/N_0 (above which the initial rise is no longer present in the $^5D_1$ decay curve) corresponds, according to the data in Fig. 4, to an intensity of about 18 μJ per pulse, in good agreement with the observation that the initial rise is still observed at 15 μJ but no more visible at 30 μJ.

The main features described above remain valid up to about 400 K. At higher temperatures, both $^5D_1$ and $^5D_0$ fluorescence decays appear to be purely exponential with the same time constant, the initial rise or the initial short decay being no more visible, as shown in Fig. 5. Most probably, this comes from the fact that the lifetime τ_1 above 400 K is shortened so as to fall in the region of the multichannel analyzer resolution (2 μs) or below. The τ_0 temperature dependence in the (250—650)-K interval is shown in Fig. 6. The ratio S_{11}/S_{02} of the integrated intensities of the $^5D_1 \rightarrow {}^7F_1$ emission to the $^5D_0 \rightarrow {}^7F_2$ one appears also for each temperature in Fig. 6. It is to be noted that the $^5D_0$ lifetime experiences a drastic decrease at temperatures above 430 K while the ratio S_{11}/S_{02} is observed to increase in the same temperature interval. The interpretation of this thermal behavior in the framework of the existing models describing radiationless processes in crystals falls out of the scope of the present paper. At the moment, these data must be considered as giving evidence of the efficiency of the $^5D_0 \rightarrow {}^5D_1$ upward radiationless transition in the Sm^{2+}:BaClF system above room temperature.

Now, we must answer the following question: why was the exponential tail with the time constant τ_0 never observed in the $^5D_1$ decay curve when pumping into the $^5D_1$ level, even at room temperature?[3,5] The initial populations of levels $^5D_1$ and $^5D_0$ under pulsed laser excitation into the $^5D_1$ level are $n_1(0)=N_1 \neq 0$ and $n_0(0)=N_0=0$, respectively.[3] Then, with the use of Eqs. (2), it is easy to show that the contribution to the population $n_1(t)$ of the exponential term with the time constant τ_0 becomes significant (at room temperature) only for times at which $n_1(t)/N_1 < 7\times10^{-3}$. Therefore, it is clear that the exponential tail with the time constant τ_0 should hardly be observed in the $^5D_1$ decay curve under these conditions. On the other hand, the situation is quite different under ultraviolet excitation, providing at room temperature a nonzero initial population of the $^5D_0$ level, owing to fast $4f^5$-$5d \rightarrow {}^5D_0$ radiationless transitions.[5] Then, the amplitude ratio ρ of the τ_0 and τ_1 components in the expression of $n_1(t)$, as derived from Eqs. (2), may be expressed in the following way:

$$\rho = \frac{P_{01}}{P_{10}} \alpha_{10} \frac{\alpha_{10} + N_0/N_1}{1 - (P_{01}/P_{10})\alpha_{10} N_0/N_1} . \tag{8}$$

Obviously, ρ increases from $(P_{01}/P_{10})\alpha_{10}^2 \sim 10^{-3}$ to infinity as N_0/N_1 increases from 0 to $P_{10}/P_{01}\alpha_{10} \sim 7\times10^2$. Thus the excitation into the $^5D_1$ level appears to be the worse way to prove that pumping by phonon annihilation into the $^5D_1$ multiplet from the $^5D_0$ lower-lying state takes place in the Sm^{2+}:BaClF system.

In addition to these measurements, we performed experiments at liquid-helium temperature, at which the contribution to the $^5D_1$ fluorescence of the $^5D_0 \rightarrow {}^5D_1$ radiationless transition is expected to be negligible. If the assumption is valid that an absorption from the $^5D_0$ state takes place promoting the Sm^{2+} ion up to a $4f^5$-$5d$ state, then the $^5D_1$ fluorescence should be observed under excitation into the $^5D_0$ state even at very low temperature. Moreover, not only the $^5D_1$ level but also the $^5D_2$ level located at 3280 cm^{-1} above $^5D_0$ should fluoresce, since it has been shown that ultraviolet excitation into $4f^5$-$5d$ states results in this system in the fluorescence of the three metastable levels $^5D_2$, $^5D_1$, and $^5D_0$ at temperatures below 90 K.[2–5] These expectations were revealed to be completely confirmed by the experiments. Indeed, the $^5D_2$ and $^5D_1$ fluorescences were observed pumping into the $^5D_0$ level at 1.5 K. Investigations in the dynamics of these anti-Stokes emissions at low temperature are under way with the aim of giving a more detailed description of the excited-state absorption process in the Sm^{2+}:BaClF system.

ACKNOWLEDGMENTS

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