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EVIDENCE OF PHONON ANNIHILATION PROCESSES IN THE EXCITED STATES OF BaClF:Sm^{2+} †

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We have found direct evidence of upward, phonon annihilation, processes in the decay patterns of two metastable states ${}^5D_0$(14 542 cm^{-1}) and ${}^5D_1$(15 878 cm^{-1}) of BaClF:Sm^{2+}. Under pulse excitation, the decay curve of the ${}^5D_1$ fluorescence includes a long tail, with a time constant equal to the lifetime of ${}^5D_0$, which appears at ~280°K and grows in intensity with temperature; finally at ~400°K both states decay with the same time constant. This finding is consistent with the thermal dependence of the ratio of the intensities of the ${}^5D_1$ to the ${}^5D_0$ flourescence.

Consider a three-level fluorescent system with levels 1, 2, and 3, indicating, respectively, the ground state and two excited (metastable) states. Assume also that the system can be optically excited by pumping into an absorption band above level 3 and that the excited centers decay from this band to level 3 by very fast radiationless processes. When excited by a sharp pulse of light, the population of level 2 decays to equilibrium according to an exponential law if the relaxation processes between the levels 3 and 2 are much faster than the lifetime of level 2. On the other hand, if the rate of these processes is of the same order of magnitude as the lifetime of level 2, the population decays according to a more complicated law which consists of the (algebraic) sum of two exponentials with characteristic time constants given by the lifetimes of levels 2 and 3. The fluorescence signal from level 2, after the end of the pulse, may present either a rise followed by an exponential decay or a double decay, the two conditions being determined by the values of the populations of levels 2 and 3 at the end of the pulse. The fluorescence signal from level 3 presents an exponential decay in any case.

If the two energy levels 2 and 3 are close enough, relaxation processes may take place among them with rates (for both the 3 → 2 and 2 → 3 processes) much faster than the intrinsic lifetimes of the two states, resulting in a "thermalized condition" for the two levels. In this condition the two levels decay to equilibrium with a common value for their decay constants, which depends on the intrinsic values of the two lifetimes, the degeneracies of the two levels, the energy gap, and the temperature.[1] Also, in this condition, if the system is under continuous optical excitation, the populations of the two levels and, consequently, the intensities of the fluorescence lines originating from them follow a Boltzmann law $e^{\Delta E/kT}$ with ΔE = energy gap. The existence of such a condition is generally mentioned as evidence of upward (2 → 3) phonon annihilation processes.

Considering now these upward (phonon annihilation) processes, it should be possible, in principle, to find direct evidence of them, in the form of a double exponential decay for the fluorescence from the upper fluorescent level 3, when their rate is comparable with the lifetime of this level. In these conditions one should be able to observe in the decaying fluorescence signal from level 3 an exponential component with time constant equal to the lifetime of level 2.

We have actually observed this phenomenon in the fluorescent system BaClF:Sm^{2+}. This system lends itself to these studies because the weak coupling of the fluorescent ion Sm^{2+} to the lattice allows the presence of three metastable states at low temperature: ${}^5D_0$ (14 542 cm^{-1}), ${}^5D_1$ (15 878 cm^{-1}), and ${}^5D_2$ (17 820 cm^{-1}). The fluorescence spectrum is due to transitions from these states to the ground-state multiplet ${}^7F_0$ to ${}^7F_4$ and is obtained by exciting the system in the strong $4f^55d$ bands. The energy level scheme along with the absorption bands is shown in Fig. 1.[2-4] All the fluorescence lines remain sharp even at very high temperatures (~10 cm^{-1} at 600°K).

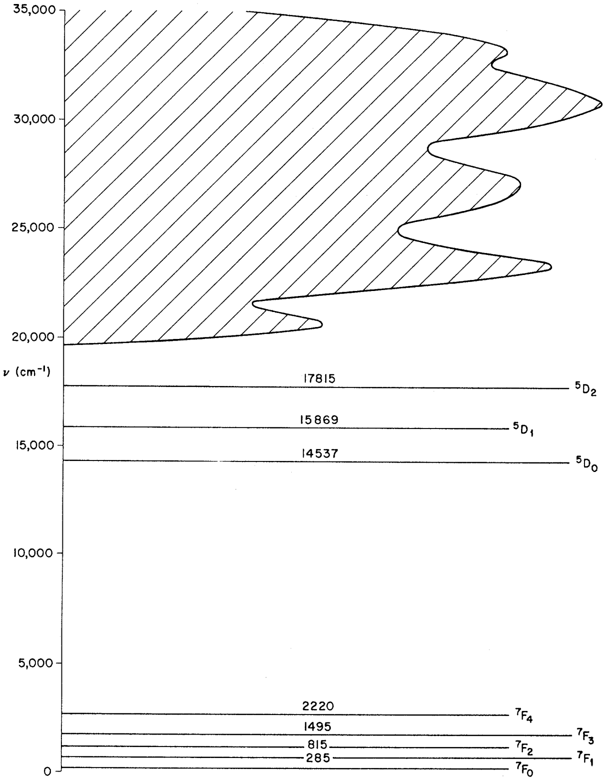

FIG. 1. Energy levels of BaClF:Sm^{2+}.

The decay patterns of the fluorescence lines, when the system is excited by a pulse of light, present evidence of $D_2 \rightarrow D_1$ and $D_1 \rightarrow D_0$ radiationless processes, most dramatically in the fluorescence from the level $^5D_0$ which up to 360°K presents a characteristic rise followed by a decay.[5,6] The time $t_{\max}$ at which the maximum in the fluorescence signal occurs is observed to be 900 and 90 μsec at 80 and 300°K, respectively, while the lifetime of the $^5D_0$ level is found to be almost temperature independent in this range with a value of 1.6 msec. The lifetime of the $^5D_1$ state is 840 μsec at 80°K and 140 μsec at 300°K.

The $D_2 \rightarrow D_1$ processes are much faster than the $D_1 \rightarrow D_0$ processes (the lifetime of the $^5D_2$ state is ~80 μsec at 80°K) despite the fact that the D_2-D_1 energy gap is larger by 714 cm^{-1} than the D_1-D_0 gap, probably due to the closeness of the $4f^55d$ bands which may enhance the probability for the $D_2 \rightarrow D_1$ radiationless decay. The fluorescence efficiencies of the three states are strongly temperature dependent with the lower states becoming more efficient as the temperature is raised: The most efficient states at 300, 80, and 15°K are $^5D_0$, $^5D_1$, and $^5D_2$, respectively. No fluorescence is observed from level $^5D_2$ above ~100°K.

As already noticed, the fluorescence signal from the $^5D_0$ state presents a rise, followed by a decay. The time $t_{\max}$ can be correlated to the presence of a second exponential with the time constant equal to the lifetime of $^5D_1$. We concentrated our study in the 250-400°K region and Fig. 2 illustrates our results.

Figure 2(a) shows the decays $^5D_0 \rightarrow {}^7F_0$ and $^5D_1 \rightarrow {}^7F_0$ at 280°K with the characteristic rise in the $^5D_0$ fluorescence. At this temperature a tail starts to appear in the $^5D_1$ fluorescence signal resulting in a double exponential. With increasing temperature (310°K), the exponential with the longer decay time in the $^5D_1$ fluoresence grows in intensity with respect to the exponential with the short decay time [Fig. 2(b)]. The decay time of the tail at any temperature is equal to the lifetime of $^5D_0$. Finally at ~375°K [Fig. 2(c)] and higher temperatures, the exponential with the short decay time is no longer present in the $^5D_1$ fluorescence and the resulting single exponential has a decay time which coincides with the decay time of $^5D_0$. The temperature dependence of the common value of the $^5D_0$ and $^5D_1$ lifetimes above 400°K, report-

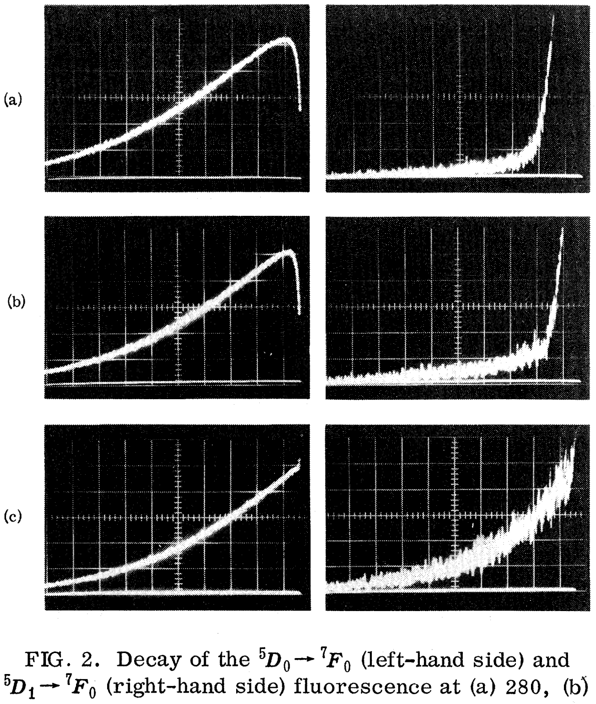

FIG. 2. Decay of the $^5D_0 \rightarrow {}^7F_0$ (left-hand side) and $^5D_1 \rightarrow {}^7F_0$ (right-hand side) fluorescence at (a) 280, (b) 310, and (c) 375°K. Sweep speed for all pictures: 500 μsec/div. Gain setting of scope is the same for pictures on the same side.

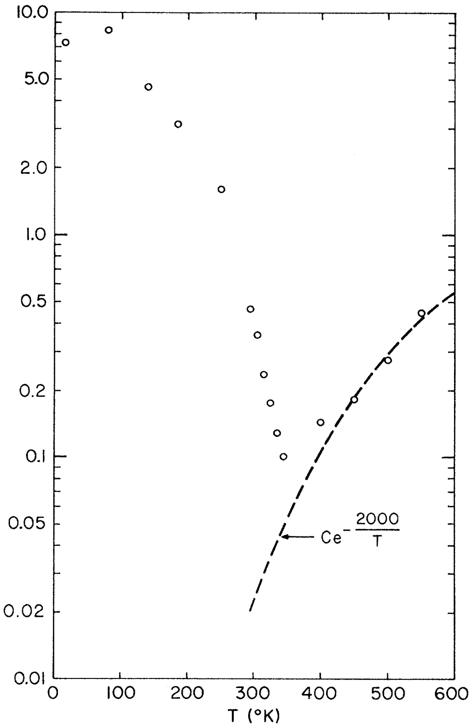

FIG. 3. Ratio of the integrated intensities of the $^5D_0 \to {}^7F_0$ to the $^5D_1 \to {}^7F_0$ fluorescence versus temperature.

ed elsewhere,[6] presents the characteristic behavior expected from thermalized levels.[1]

To substantiate further our observations we measured the ratio of the integrated intensities of the $^5D_1 \to {}^7F_0$ to the $^5D_0 \to {}^7F_0$ fluorescence, from 15 to 600°K, with the system under continuous optical excitation. The results are reported in Fig. 3. The increase in the ratio up to ~80°K is due to the increase of the $D_2 \to D_1$ decay rate in that region. Above 80°K the ratio decreases because of the depopulation of $^5D_1$ through $D_1 \to D_0$ decay (we notice here that the $^5D_0$ lifetime is almost constant and equal to ~1.6 msec up to 300°K). At about 330°K a turning point occurs and the ratio starts increasing with temperature, because of the fact that upward phonon annihilation processes become more and more relevant. Finally from ~400°K up the ratio follows a Boltzmann law, indicating the presence of the thermalization condition. This, on the other hand, is the temperature at which the $^5D_0$ and $^5D_1$ decays start presenting equal time constants.

Both the pulsed-fluorescence and the continous-fluorescence data provide direct evidence of phonon annihilation processes in the excited states of BaClF:Sm^{2+}.

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TWO-PHOTON ABSORPTION SPECTRUM OF CuCl

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Two-photon measurements were done on single crystals of CuCl at 20°K in an energy range from 3.2 to 4.3 eV. For the first time sharp exciton lines are found in a two-photon spectrum. A detailed study of the polarization dependence yields symmetry assignments of the exciton states.

Two-photon spectra have first been measured by Hopfield and Worlock[1] on KI and CsI; subsequently other ionic crystals (TlCl,[2] RbBr, RbI, KBr, and NaBr[3]), a semiconductor (CdS[4]), and a molecular crystal (anthracene[5]) were investigated. The spectra of CdS and the ionic crystals show a very similar behavior: The two-photon spectra start in the region of the band gap and rise towards higher energies without indicating any pronounced structure. No resolved exciton lines have been seen in these spectra. There is some structure found in the

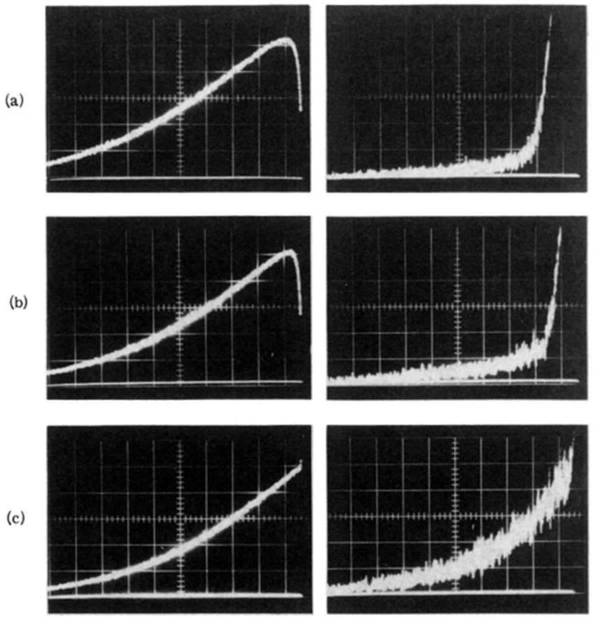

FIG. 2. Decay of the $^5D_0 \rightarrow {}^7F_0$ (left-hand side) and $^5D_1 \rightarrow {}^7F_0$ (right-hand side) fluorescence at (a) 280, (b) 310, and (c) 375°K. Sweep speed for all pictures: 500 μsec/div. Gain setting of scope is the same for pictures on the same side.