absorption band in the visible region for solutions containing the cryptate and the quencher. Spectrophotometric and electrochemical analysis show that 1:1 complexes are formed with stability constants of the order of 10^2 l mol^{-1}.

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B17

Dependence of the $^5D_0 \rightarrow {}^5D_1$ Fluorescence Dynamics *Versus* the Optical Pumping Frequency in Sm^{2+}:BaClF

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Very recently, the role of the $^5D_0 \rightarrow {}^5D_1$ upwards radiationless transition in the de-excitation mechanisms of the Sm^{2+} ion in BaClF at temperatures ranging from 295 to 650 K was clearly established [1]. Using selective pulsed laser excitation into the first metastable excited state $^5D_0$ (14533 cm^{-1}), the fluorescence of the $^5D_1$ multiplet located at 1339 cm^{-1} above $^5D_0$ was detected. Both $^5D_1$ and $^5D_0$ fluorescence at long times after the laser pulse were observed to decay exponentially with the same time constant (~1.5 ms at room temperature) characteristic of the $^5D_0$ lifetime in this material, as shown in Figs. 1a) and b). This experiment confirms that a thermalization process between levels $^5D_0$ and $^5D_1$ takes place in this system, as observed 16 years ago using an ultraviolet excitation promoting the Sm^{2+} ion up to $4f^5$-5d states [2, 3]. Surprisingly enough, the $^5D_0$ and $^5D_1$ fluorescence decays under excitation into the $^5D_1$ level do not bear evidence of such a thermalization process, as shown in Figs. 1c) and d), the $^5D_1$ fluorescence being observed to decay exponentially with a time constant equal to the intrinsic $^5D_1$ lifetime (~150 μs at room temperature). Moreover, all the measurements we performed in previous works pumping the system either in the $^5D_1$ or $^5D_2$ level were found to be consistent with the assumption that the $^5D_0 \rightarrow {}^5D_1$ radiationless transition did not contribute signi-

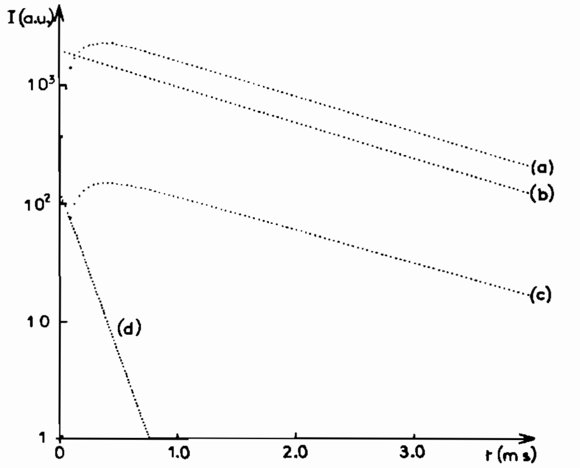

Fig 1. Fitted decay-curves of the $^5D_0$ (b, c) and $^5D_1$ (a, d) fluorescences under selective excitation into the $^5D_0$ (a, b) and $^5D_1$ (c, d) levels.

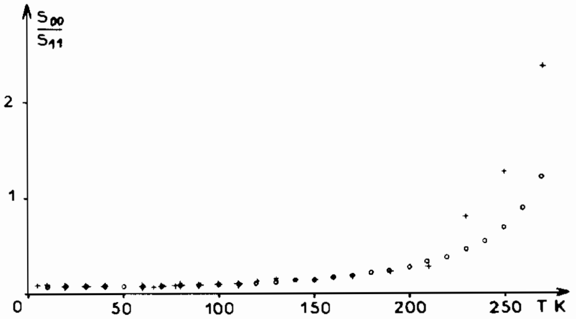

Fig. 2. Comparison between the temperature dependences of the ratio S_{00}/S_{11} of the integrated intensities of the $^5D_0 \rightarrow {}^7F_0$ emission to the $^5D_1 \rightarrow {}^7F_1$ one in the spectra recorded under pulsed selective excitation into the $^5D_1$ level (○) and continuous ultraviolet excitation (+).

ficantly to the optical properties of the Sm^{2+}: BaClF system at temperatures up to 300 K [4–6]. The physical explanation for these discrepancies lies in the fact that the feeding of levels $^5D_0$ and $^5D_1$ during the excitation pulse depends strongly on the pumping conditions [1]. Obviously, the role of the $^5D_0 \rightarrow {}^5D_1$ radiationless transition will be enhanced if the population of the $^5D_0$ state at the end of the pulse is significant, as is the case for the $^5D_0$ pumping. On the other hand, the contribution of this transition will be reduced if the $^5D_0$ population remains equal to zero during the excitation pulse, as is the case for the $^5D_1$ or $^5D_2$ pumping. Under ultraviolet excitation, the feeding of the $^5D_0$ state during the pulse is ensured by fast non radiative processes connecting the $4f^5$-5d states directly to the $^5D_0$ state at temperatures above 200 K as it clearly appears from the comparison between the temperature dependences of the ratio S_{00}/S_{11} of the integrated intensities of the $^5D_0/^7F_0$ emission to the $^5D_1 \rightarrow {}^7F_1$ one in the spectra recorded under selective excitation into the $^5D_1$ level on one hand, and ultraviolet excitation on the other hand (Fig. 2).

Thus, the thermalization near room temperature between two rare-earth levels separated by an energy gap of several times the maximum phonon frequency in the crystal (294 cm^{-1} in BaClF) [6] may be observed or not, depending on the optical pumping frequency. Similar investigations in other rare-earth systems such as Eu^{3+} doped materials, with larger $^5D_1 - {}^5D_0$ gaps and higher $4f^5$-5d state energies should be of interest to complement this observation.

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B18

Mechanisms for f–f Transition Probabilities in Lanthanide Coordination Compounds

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The Laporte-forbidden transitions of Ln(III) coordination compounds acquire a first-order electric-dipole probability from transient dipoles induced in the ligand groups by an allowed even-multipole electric moment of the f–f excitation, and by the mixing of the f–f with f–d and f–g electron promotions under the electrostatic field of the ligands. Applied initially to Ln(III) complexes containing monoatomic ligands which have an effective isotropic polarizability the ligand-polarization mechanism is found to depend, on extension to the corresponding polyatomic ligand cases, upon the anisotropy of the ligand polarizability tensor in complexes belonging to the higher non-centric symmetries. The electrostatic field and the ligand polarization mechanisms make complementary intensity contributions to the f–f transitions of a given Ln(III) complex type, dependent upon the rank of the leading electric multipole moment. The polarization mechanism contributes principally to the intensities of the ligand-hypersensitive 2^2-pole f–f transitions, whereas the electrostatic mechanism is predominant for the 2^6-pole transition intensities, and makes the more important contribution in the 2^4-pole cases.

B19

Absorption and Fluorescence Spectra of Europium(III) Compounds in Non-Aqueous Solutions

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The absorption and fluorescence spectra of Eu(III) compounds were investigated at room temperature in different non-aqueous solutions.