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Two-photon Excitation of the Sm^{2+} Ion in BaClF*

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The advent of high power laser sources has opened up the possibilities of observing two-photon processes in crystals. We report here the first measurements of two-photon excitation spectra of the Sm^{2+} fluorescence in BaClF. The one-photon spectroscopy of the Sm^{2+} ion in this material has been investigated a few years ago and the energies and symmetries of the Stark components belonging to the ^7F_J ($J = 0$ to 6) and ^5D_J ($J = 0$ to 2) multiplets of the $4f^6$ ground configuration are well known [1]. It is thus tempting to look at the two-photon absorption intraconfigurational transitions which may be induced in this system and to see if the theoretically predicted selection rules are valid.

The experimental set up for single beam two-photon excitation of the Sm^{2+} ion in the ^5D_J states ($J \leqslant 2$) is shown in Fig. 1. The pulsed laser beam (pulse duration: 15 ns) at the output of a YAG:Nd^{3+}

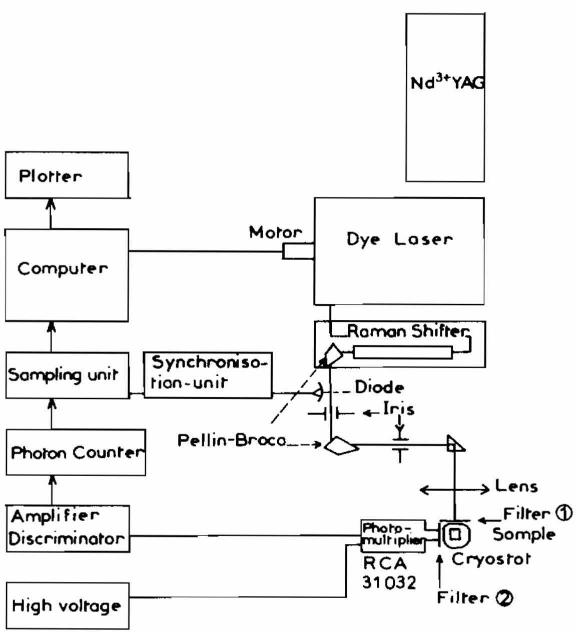

Fig. 1. Experimental set up for two-photon excitation spectrum measurements (single beam arrangement).

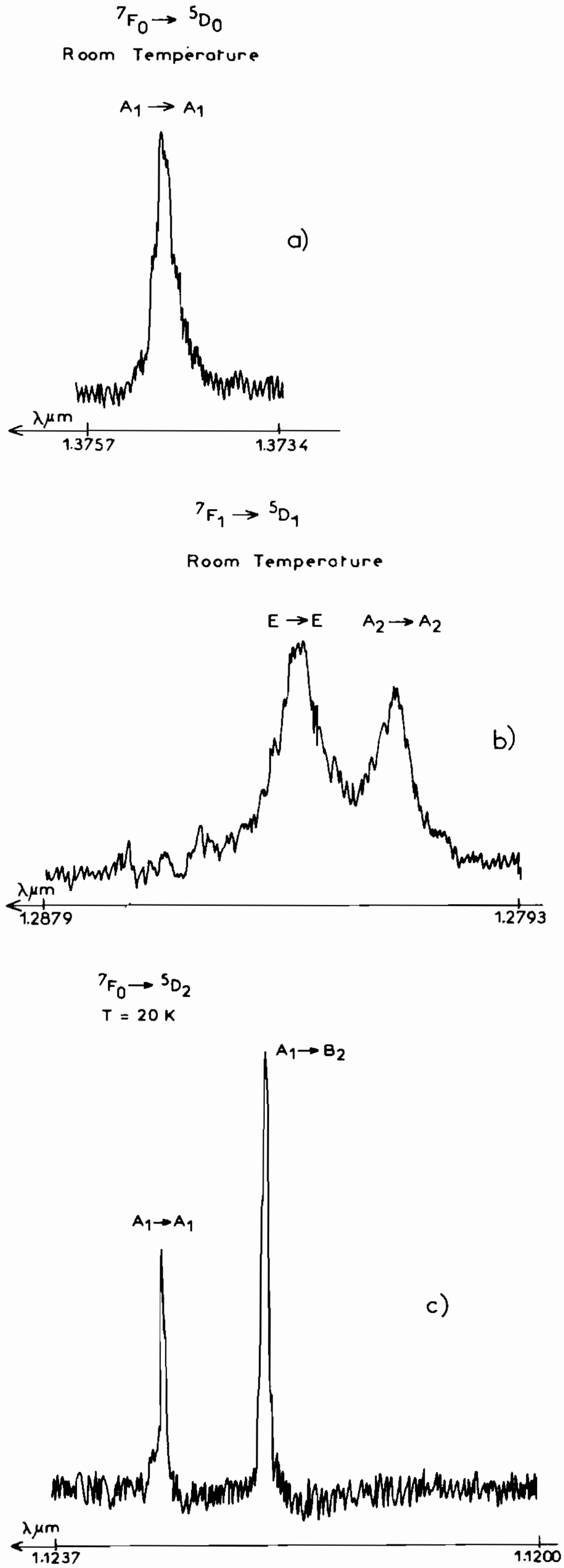

Fig. 2. Details of the two-photon excitation spectra of the $^5D_0$ (a), $^5D_1$ (b) and $^5D_2$ (c) fluorescences.

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pumped dye laser from Quantel (Datachrom model) was passed through a hydrogen Raman cell which delivered Stokes radiations corresponding to photon energies shifted by 4155 cm^{-1} (Stokes1) and 8310 cm^{-1} (Stokes 2). The Stokes 2 radiations of the laser beam obtained with (a) DCM (4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyrl-4H-pyran), (b) Rhodamine 640 and (c) the dye mixing Rh 590/610 provided suitable infrared sources for two-photon excitation in the $^5D_0$, $^5D_1$ and $^5D_2$ states, respectively. The sample of dimensions $5 \times 4 \times 1$ mm^3 was mounted in a liquid helium cryostat with its *c* axis parellel to the direction of the excitation beam. Appropriate filters were used to select the induced fluorescence. Nevertheless, its detection required the aid of time-resolved spectroscopy techniques in order to eliminate the part due to the scattered laser beam light from the signal delivered by the photomultiplier.

The $^7F_0 \rightarrow {}^5D_0$, $^7F_1 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_2$ transitions appearing in the two-photon excitation spectra of the $^5D_0$, $^5D_1$ and $^5D_2$ fluorescences are presented in Figs. 2a, b and c, respectively. These three transitions are spin-forbidden but the mixing of states due to the spin–orbit interaction is expected to break the $\Delta S = 0$ rule as observed for one-photon transitions. In addition, the observation of the $^7F_0 \rightarrow {}^5D_0$ transition may be due either to *J*-mixing ($J = 0 \rightarrow J = 0$ transitions are forbidden if *J* remains a good quantum number for both one- and two-photon processes), or to the contribution of a third-order mechanism involving the spin–orbit interaction solely, as stated by Judd and Pooler [2]. The assignment of Stark components appearing in the spectra of Fig. 2 is easy since the energy and symmetry of the Stark levels are known from one-photon spectroscopy. The assignment is in good agreement with the selection rules predicted by Bader and Gold in the case of a C_{4v} symmetry for the polarization vector of the laser beam perpendicular to the *c*-axis [3]. None of the $A_1 \rightarrow E$, $A_2 \rightarrow E$ and $A_1 \rightarrow A_2$ transitions which are present in the similarly polarized one-photon spectra appear. This observation also explains that two-photon excitation in the $^5D_1$ states does not occur at low temperature under these experimental conditions. The $^7F_0 \rightarrow {}^5D_2$ spectrum is expected to exhibit two $A_1 \rightarrow B$ components unless the polarization vector belongs to a σ_v or σ_d plane. The occurrence of the sole $A_1 \rightarrow B_2$ component may indicate that this last condition is fulfilled in our experiments.

In conclusion it is to be noted that excitation beam energies as high as 450 μJ per pulse were required to produce detectable fluorescent signals and that radiation damages were observed to occur in the crystal above 500 μJ/pulse.

References

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