

COMPETITIVE EXCITATION MECHANISMS FOR THE BLUE FLUORESCENCE IN  $\text{CdF}_2:1\% \text{Er}^{3+}$ 

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We report direct experimental evidence of the coexistence of two distinct optical double-resonance processes resulting in the blue ( $0.41\text{-}\mu$ ) fluorescence in  $\text{CdF}_2:1\% \text{Er}^{3+}$ . Our experiments contradict the conclusions of Feofilov and Ovsyankin who claim that the cooperative process properly describes long-wavelength activated visible fluorescence.

The process by which short-wavelength fluorescence is induced in rare-earth-doped single crystals has recently become a subject of dispute. The Bloembergen quantum counter<sup>1</sup> (fluorescence as the result of successive absorption in one center) has generally been invoked to explain the great variety of fluorescence schemes reported—this, despite many reports of ion pair processes.<sup>2-5</sup>

In several recent publications,<sup>6,7</sup> however, Feofilov and Ovsyankin deduce from lifetime data of infrared-activated visible fluorescence in  $\text{Er}^{3+}$  that this explanation (successive absorption in one center) must be regarded as erroneous. Instead they propose a “cooperative process” whereby the excitation energy is absorbed by ground-state electrons of separate ions. Migration of the excitation energy can then occur resulting in a populated pair state from which fluorescence may occur. The excitations need not be of the same energy; however, there must exist appropriate transitions from the ground state that allow absorption of the infrared or optical radiation.

In the case of the quantum counter, where visible fluorescence is produced by summing of the excitation energy via sequential absorption in one center, the first photon populates a metastable level above the ground state. The second photon induces a transition to a higher metastable level in the same ion from which fluorescence occurs.

We report a set of experiments which offers direct evidence that, in fact, both processes do occur, at least in one of the ions studied ( $\text{Er}^{3+}$ ). Since quantum counter action is the result of two-step excitation in one center, it is possible to identify this process by determining whether or not the excitations which produce fluorescence involve one absorption transition from the ground

state and one between excited states of the same ion. Similarly, the cooperative process can be identified if the excitations which produce fluorescence can be shown to be the result of two absorption transitions from the ground state—hence in separate ions.

One simple experiment which makes this distinction (between excited and ground-state absorption transitions) is a variant<sup>8</sup> of the Varsanyi<sup>9</sup> optical-double-resonance experiment. The population of ions excited to the first excited state is modulated with a chopped infrared (ir) beam. A monochromatic “monitor” beam is scanned in wavelength and the transmission through the crystal is monitored. When the monitor beam matches the energy difference between the first excited and a higher excited state or a transition from the ground state to an excited state, modulation in the transmitted flux of the monitor beam at the chopping frequency is detected. The phase of this signal with respect to the chopped ir flux positively discriminates<sup>10</sup> between absorption from the first excited state and from the ground state.

By comparing the “absorption spectrum” of the crystal obtained in this manner with the spectrum of pump radiation inducing fluorescence, it is possible to distinguish unambiguously between excitation via successive absorption of two photons in one center and cooperative sensitization via the interaction of two separate excited ions.

The rectangular crystals ( $7 \times 7 \times 15 \text{ mm}^3$ ) buffed on all six sides were purchased from Litton Industries. The crystal, EMR S-20 photomultiplier tube, lenses, and appropriate filters were mounted in a light-tight box. The monitor beam originating from a  $3200^\circ\text{K}$  quartz-iodine tungsten lamp (dc) was focused onto the entrance slit of a modified (resolution  $25 \text{ \AA}$ )  $0.25\text{-m}$  Jarrell-Ash

monochromator. The infrared pump was a 1000-W DFK tungsten lamp chopped at 15 cps by a Princeton Applied Research Corporation model BZ-1 chopper. For absorption measurements the dc monitor beam was applied perpendicular to the ir source and focused onto the crystal and phototube. For fluorescence spectra a 1000-W Xe arc lamp was used for the visible pump and was applied along the axis of the ir source. The photomultiplier output was amplified by a Princeton Applied Research Corporation HR-8 lock-in amplifier using a reference signal derived from the infrared chopper.

Figure 1(a) is the normalized absorption spectrum of  $\text{CdF}_2:1\%\text{Er}^{3+}$  taken with the same apparatus used for the double-resonance measurements (resolution  $25 \text{ \AA}$ ). The spectrum shown in Fig. 1(b) was obtained by chopping  $1.45\text{-}\mu$  radiation and detecting the modulation (at the chopping frequency) of the monitor beam as it was swept in wavelength. The regions of indicated absorption are the result of the periodic modulation in the transmission of the monitor beam through the crystal as the result of the periodic modulation of the population of ions in the ground or first excited state.

The polarity differences in the signals of Fig. 1(b) are due to the change in phase of the signals with respect to the chopped ir beam. Signals with indicated positive polarity ( $\alpha, \gamma, \eta$ ) are reversed in phase with respect to the chopped beam

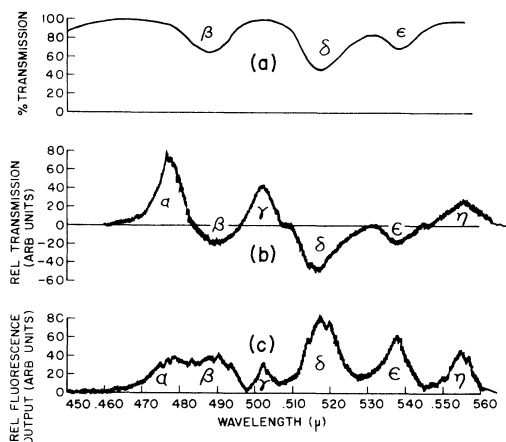


FIG. 1. (a) Normalized absorption spectrum of  $\text{CdF}_2:1\%\text{Er}^{3+}$ . (b) Double-resonance absorption spectrum. Positive polarity signals are the result of absorption between excited states; negative polarity signals are the result of both chopped ir and visible monitor beams exciting ions from the ground state. (c) Double-resonance excitation spectrum. The amplitude of  $0.41\text{-}\mu$  fluorescence is displayed versus pump wavelength.

and hence are the result of absorption between excited states. Similarly, those with negative polarity ( $\beta, \delta, \epsilon$ ) are the result of both ir and monitor beams exciting ions from the ground state.

Figure 1(c) is a spectrum of pump radiation including fluorescence obtained by chopping  $1.4\text{-}\mu$  radiation, scanning in wavelength an optical pump, and detecting narrow-band fluorescence centered at  $0.41 \mu$ . The existence of a fluorescence output when the pump is inducing transitions between excited states ( $\alpha, \gamma, \eta$ ) is proof that the signal is due to successive absorption of two photons in one center (quantum counter). The existence, however, of a fluorescence signal when the pump is exciting ions from the ground state ( $\beta, \delta, \epsilon$ ) is definite proof that the excitation is the result of the interaction of two separate excited ions. Figure 2 is an energy level diagram of the pertinent levels of  $\text{CdF}_2:1\%\text{Er}^{3+}$ . The double arrows ( $\alpha, \gamma, \eta$ ) indicate quantum counter action; the single arrows ( $\beta, \delta, \epsilon$ ) indicate the transitions involved in the cooperative sensitization process.

We believe that our data offer direct evidence of the coexistence of two distinct mechanisms of optically activated visible fluorescence in  $\text{Er}^{3+}$ . In contradiction to the conclusions stated in Refs. 6 and 7, the fluorescence schemes observed

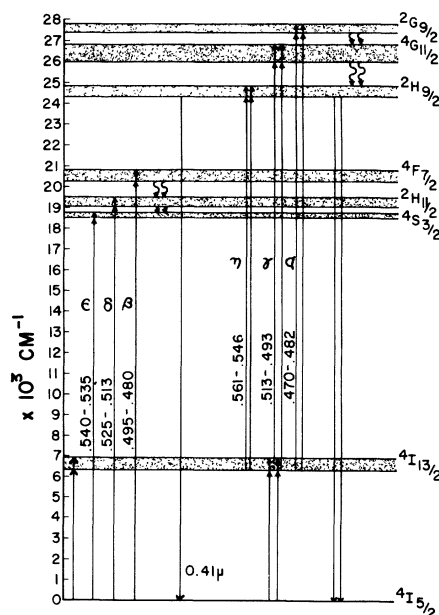


FIG. 2. Energy level diagram of  $\text{CdF}_2:1\%\text{Er}^{3+}$  showing pertinent levels. Single arrows indicate absorption transitions involved in cooperative sensitization; double arrows indicate the levels involved in quantum counter action. Only the levels of interest have been included. Wavy lines indicate nonradiative transitions.

occur with approximately equal quantum efficiencies (order of  $10^{-6}$  visible photons per incident ir photon) for the two mechanisms in this ion. Moreover, preliminary studies in  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  indicate that successive absorption in one center is the dominant mechanism by at least three orders of magnitude (the cooperative process was not, in fact, observed).

Extreme care must be taken before attributing a particular mechanism to these double-resonance experiments. Studies such as described in this paper and in Refs. 6 and 7 are needed to identify the actual mode(s) of excitation properly.

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<sup>10</sup>If the monitor beam is resonant with a transition between the first and a higher excited state, the transmitted flux detected by the photomultiplier will decrease in the presence of the ir beam which populates the first excited state. In the absence of the ir flux the population of the first excited state vanishes, and excited state absorption can no longer occur. Hence, the transmitted flux increases. In this sense, the undulation of the monitor beam when excited state absorption is occurring is reversed in phase with respect to the chopped ir flux. If, on the other hand, the monitor beam is resonant with an absorption transition from the ground state, the presence of the ir pulse increases the transmitted flux of the monitor beam. This is a result of the fact that the ir radiation decreases the population of ions in the ground state, resulting in a decrease in the absorption of the monitor beam. In the absence of the ir flux the attenuation of the monitor beam increases (the transmitted flux decreases). Thus, when the monitor beam is inducing transitions from the ground state, the absorption signal obtained in this manner is in phase with the chopped ir flux.

<sup>11</sup>L. Esterowitz and E. Chicklis, to be published.

## THE INFLUENCE OF LEVEL DEGENERACY ON THE SELF-INDUCED TRANSPARENCY EFFECT\*

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Self-induced transparency effects are examined in an absorbing medium having degenerate optical transitions. Undistorted propagating light pulses exist under restrictive conditions for  $j \rightleftharpoons j$  transitions ( $j > 0$ ) and for  $0 \rightleftharpoons 1$  and  $\frac{1}{2} \rightleftharpoons \frac{3}{2}$ . Pulses which propagate without energy loss for any transition  $j \rightleftharpoons j'$  also include zero-degree pulses defined as  $\int \mathcal{E}(z, t) dt = 0$ .

A recent publication<sup>1</sup> has described conditions under which an electromagnetic radiation pulse can propagate undistorted and without energy loss through a normally absorbing medium. Specifically, the effect was shown to occur in a system consisting of a single pair of energy levels coupled to the field by a dipole matrix element. This self-induced transparency effect was demonstrated with the  $4A_2(\pm\frac{1}{2}) \rightleftharpoons \bar{E}(2E)$  transition of the  $\text{Cr}^{3+}$  ion in ruby<sup>1</sup> and was subsequently reported<sup>2</sup> to have been observed with an unidentified  $10.6\text{-}\mu$  rotation-vibration transition in gaseous  $\text{SF}_6$ . The purpose of this Letter is to indicate that the self-induced transparency effect is modified considerably when there are several

pairs of levels with overlapping transition frequencies and matrix elements of different values. An important example is that of dipolar transitions between states having angular-momentum quantum numbers  $j$  and  $j'$ , where either  $j$  or  $j'$  or both are greater than one. In the absence of a Stark or Zeeman perturbation, the magnetic sublevels  $m_j$  (or  $m_{j'}$ ) are degenerate and the dipole matrix elements  $\mu_{jj'm_j m_{j'}}$  depend on  $m_j$  and  $m_{j'}$ . It is found below that the pulse shape and its propagation behavior depend strongly on the angular-momentum quantum numbers associated with the transition. The results show generally that for a  $j \rightleftharpoons j \pm 1$  transition ( $j$  arbitrary) an undistorted pulse propagating without attenuation