

# Nonlinear delocalization of excited states in disordered crystals

V. V. Ovsyankin and A. A. Fedorov

*S. I. Vavilov State Optics Institute*

(Submitted 30 December 1981; resubmitted 1 February 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **35**, No. 5, 199–201 (5 March 1982)

Optical pumping above a certain critical level causes the luminescence-excitation spectrum of crystals of a disordered tysonite to assume the form expected for systems which have undergone Anderson delocalization [P. W. Anderson, *Phys. Rev.* **109**, 1492 (1958); *Proc. Nat. Acad. Sci. USA* **A69**, 1097 (1972)].

PACS numbers: 78.55. — m, 78.45. + h

We have studied excited states of the disordered tysonite  $\text{SrYb}_2\text{F}_8$  which are genetically related to the excitation of a  $\text{Yb}^{3+}$  ion in an unfilled  $4f^{13}$  configuration (this is a transition between lowest-lying components of the crystal splitting of the  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$  terms). The inhomogeneous broadening of the states involved in the optical transition results from a spread of the local crystal fields caused by the random distribution of cations and of anion vacancies among the system of regular structural sites of tysonite,  $\text{LaF}_3$ . The half-width of the inhomogeneous broadening,  $|\Delta|$ , is  $\Delta \cong 35 \text{ cm}^{-1}$  (Fig. 1). The delocalizing interaction is caused primarily by the quadrupole-quadrupole term in the multipole expansion of the electrostatic interaction. At the minimum separation of  $\text{Yb}^{3+}$  ions allowed by the crystal structure, the magnitude of the interaction is  $V_{qq}(R_{\min}) \equiv V \cong 5 \text{ cm}^{-1}$ . Correspondingly, we have a ratio  $\Delta/V = 7$ . Comparing this value with numerical calculations of the critical values from the Anderson model for three lattices,<sup>2</sup> we may expect that the central state-density region is filled by a zone of delocalized states, while the edges of the distribution are filled by localized states, which are believed<sup>3</sup> to be separated from the delocalized states by mobility thresholds  $\omega_c$  and  $\omega'_c$  (Fig. 1). An important distinction between our system (and most other real systems) and the Anderson model is that this model ignores the electron-phonon interaction, which causes an energy exchange between nonresonant electronic states; this exchange is usually very effec-

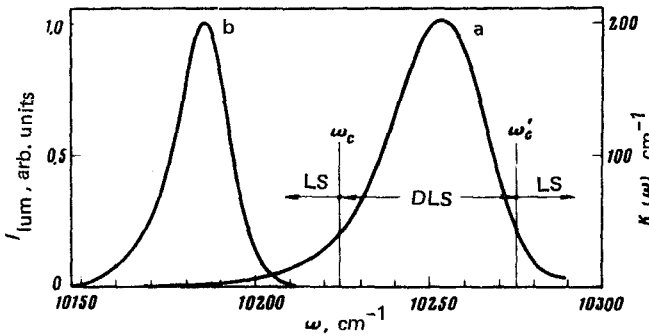


FIG. 1. a—Absorption spectrum; b—luminescence spectrum of  $\text{SrYb}_2\text{F}_8$  at  $T=1.8$  K.

tive. In particular, the intermode electron-phonon exchange in  $\text{SrYb}_2\text{F}_8$  causes a rapid relaxation of the excited states into the low-energy wing of the distribution at  $T=1.8$  K, so that the steady-state luminescence is determined by transitions in the system of localized states in the low-energy wing, regardless of the excitation region (Fig. 1).

To show that the intermode relaxation radically changes the picture of events associated with the propagation of delocalized excited states, we need detectors which are sensitive to the (spatial) diffusion of excited states. As such detectors we will use a small number of point defects which quench the luminescence ( $N_Q \ll 10^{-8} N_{\text{Yb}}$ ); these defects effectively convert the excitation energy of adjacent ytterbium ions into the energy of the phonon subsystem. At  $T=300$  K the rate of the quenching caused by the thermally activated diffusion of excited states to these quenching defects is  $\gamma_Q = 3 \times 10^4 \text{ s}^{-1}$ , considerably higher than the rate of radiative transitions,  $\gamma_R = 6 \times 10^2 \text{ s}^{-1}$  (Ref. 4).

At  $T=0$  K, any effective (spatial) transport of energy would have to occur in the system of delocalized states. If we ignore the intermode relaxation, we may expect that the quantum luminescence yield of our system will change abruptly at low temperatures, from a value near unity for excitation in the region of localized states to a value on the order of  $\gamma_R/\gamma_Q = 5 \times 10^{-2}$  for excitation in the region of delocalized states. In a preliminary experiment we studied the dependence of the luminescence intensity of  $\text{SrYb}_2\text{F}_8$  at  $T=1.8$  K on the frequency of the exciting light with steady-state excitation (the exciting light came from a DKsR-150a lamp and was passed through a DFS-24 monochromator). We observed no significant deviation of the excitation spectrum from the absorption spectrum of the crystal. This agreement means that either there are no delocalized states in the crystal or the excited states created in the region of the delocalized states relax more rapidly to localized states than they interact with quenching centers. If the latter is the case, then the reservoir of localized states plays the role of a dissipative subsystem with respect to coherent energy transport through the zone of delocalized states; the interaction with this dissipative subsystem limits the time and radius of the coherent diffusion. An important point is that the localized states can hold only a finite amount of energy, and in filling them we may suppress the time variation of the delocalized states associated

with the intermode relaxation and thereby control the coherent-diffusion radius of excited states, increasing it to a value determined by the shorter of the times  $\gamma_Q^{-1}$  and  $\gamma_R^{-1}$ .

The following experiment was carried out to demonstrate this possibility: The beam from a tunable pulsed dye laser (pulse length of 30 ns, pulse energy of 3 mJ, spectral width of  $0.5 \text{ cm}^{-1}$ , and tuning range of 930-1000 nm) was passed through a calibrated liquid filter ( $\text{H}_2\text{O} + \text{CuSO}_4$ ) and focused on the sample (the spot diameter was 0.1 mm). The sample, a flat wafer  $20 \mu\text{m}$  thick (the optical density at the absorption maximum was 0.4), was held in a cryostat with liquid helium ( $T = 1.8 \text{ K}$ ) directly behind a diaphragm  $50 \mu\text{m}$  in diameter. This arrangement resulted in a uniform excitation over the volume of the crystal. The emission from the sample was projected on the photocathode of an FÉU-83 photomultiplier by a lens whose central region was masked to prevent direct transmission of the exciting light to the photomultiplier. The output current from the photomultiplier was fed to an oscilloscope and to an integrating voltmeter with an integration time constant  $\tau = 10\gamma_R^{-1}$ . In each series of measurements we varied the exciting wavelength at steps of 0.1 nm, holding the excitation intensity constant. As a result, we recorded "excitation spectra"  $I(\omega)$ , i.e., spectral curves of the intensity of the emission of the sample, integrated over the emission spectrum and over the time. At excitation densities below the critical value ( $\Lambda_{\text{cr}}$ ), the excitation spectra were identical to the absorption spectra,  $K(\omega)$ , within the experimental error. Correspondingly, the spectrum of the quantum yield, defined as the ratio  $\eta(\omega) = I(\omega)/K(\omega)$ , is constant and does not exhibit the jumps which would imply coherent diffusion of delocalized excited states toward quenching centers. At  $\Lambda \geq \Lambda_{\text{cr}}$  the excitation spectrum changes sharply, assuming the typical form shown in Fig. 2 for the particular value  $\Lambda = 2\Lambda_{\text{cr}}$ . Shown for comparison here is a spectrum recorded at  $\Lambda = 0.5\Lambda_{\text{cr}}$ . Correspondingly, the spectrum of the quantum yield takes the form expected for systems which have undergone an Anderson delocalization (Fig. 2).

Working from these results, we can draw the following picture of this new critical effect: At  $\Lambda < \Lambda_{\text{cr}}$  the delocalized excited states relax into the region of localized states, at a rate exceeding the rate of the coherent diffusion toward the quenching centers. At  $\Lambda \geq \Lambda_{\text{cr}}$ , some of the excitation energy on the delocalized excited states is expended on populating localized states; the latter become filled to the extent that the lifetime of the excited states remaining in the zone of delocalized states increases

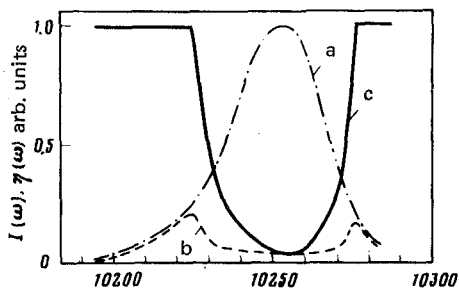


FIG. 2. a—Excitation spectrum  $I(\omega)$  at  $\Lambda = 0.5\Lambda_{\text{cr}}$ ; b— $I(\omega)$  at  $\Lambda = 2\Lambda_{\text{cr}}$ ; c— $\eta(\omega)$ , also at  $\Lambda = 2\Lambda_{\text{cr}}$ .

to a value sufficient for the onset of coherent quenching. Since the onset of coherent quenching is preceded by a filling of the localized states of the low-energy wing, i.e., since a substantial density of excited states is produced, the stage is set for *avalanche quenching of the luminescence*<sup>4</sup>: a thermally activated quenching stimulated by the phonons formed in the course of the coherent quenching. As a result, the integrated emission intensity in the case of excitation in the zone of delocalized states falls below the level corresponding to excitation at the delocalization threshold,  $\omega_c$  (Fig. 2).

The critical nature of the effects related to the saturation of intermode relaxation in systems with Anderson-delocalized excited states might find practical applications.

We wish to thank I. G. Podkolzina, T. S. Semenova, and L. F. Koryakina for growing the crystals used in these experiments.

1. P. W. Anderson, *Phys. Rev.* **109**, 1492 (1958); *Proc. Nat. Acad. Sci. USA* **A69**, 1097 (1972).
2. D. Weaire and V. Srivastava, *Commun. Phys.* **2**, 73 (1977).
3. N. G. Mott, *Adv. Phys.* **16**, 49 (1967).
4. V. V. Ovsyankin and A. A. Fedorov, *Opt. Spektrosk.* **49**, 195 (1980) [*Opt. Spectrosc. (USSR)* **49**, 106 (1980)].

Translated by Dave Parsons

Edited by S. J. Amoretty