

# Measurement of the parameters of nonresonant interactions of rare-earth ions in condensed media by selective observation of the luminescence kinetics on the line wings

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We observed in experiment an anomalous behavior of the kinetics of the decay of luminescence of rare-earth (RE) impurity ions in condensed media by selective observation on the wings of the inhomogeneously broadened lines at low temperatures. On the basis of this effect, a method is proposed for measuring the parameters of nonresonant interactions of RE ions and of their dependence of the phonon that takes part in the process. These dependences are obtained for  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$  ions in phosphate glasses.

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The mechanisms of nonresonant interactions with participation of phonons remain as before among the most obscure questions of physics of nonradiative transfer of electronic excitation energy between impurity rare-earth ions (REI) in condensed media. Several possible mechanisms of such interactions have been proposed in theoretical papers<sup>[1–3]</sup> and lead, in particular, to different dependences of the probability of elementary transfer act on the energy of the emitted (absorbed) phonon. However, attempts to determine experimentally these dependences did not yield unambiguous results.<sup>[4,5]</sup>

We have investigated experimentally the luminescence kinetics of REI at low temperatures and under pulsed photoexcitation, as functions of the observation wavelength  $\lambda_{\text{obs}}$  within the limits of the inhomogeneously broadened line (IBL) corresponding to a transition between the lower Stark components of the metastable and ground levels. The measuring setup included the following: a pulsed excitation source AG:Nd<sup>3+</sup> laser of the LTI PCh-8 type, second and fourth harmonics), an optical luminescence crystal, a DFS-12 double monochromator [dispersion 5(10) Å/mm], a cooled photomultiplier (FÉU-83 or RCA 8852), a photon-counting system with a time—multichannel analyzer ORTEC 6240A, operating in the time-scanning regime (1024 memory channels, time resolution 10 μsec/channel), and a minicomputer for the data reduction.

The optics of the investigations were concentration series of silicate, phosphate, borate glasses, activated with the ions Nd<sup>3+</sup>, Eu<sup>3+</sup>, Sm<sup>3+</sup> (0.1–15 wt.%) or Nd<sup>3+</sup> (20%) and Yb<sup>3+</sup> (0.1–10 wt.%), as well as the crystals  $\text{Na}_5\text{Nd}_{(1-x)}\text{Yb}_x(\text{MoO}_4)_4$  ( $x=0.1-0.4$ ) and frozen inorganic liquids  $\text{POCl}_3:\text{SnCl}_4$  with Nd<sup>3+</sup> admixture (3

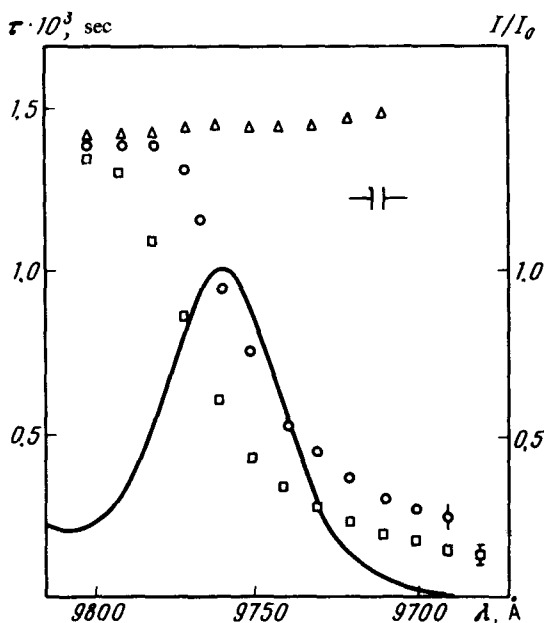


FIG. 1. Characteristic luminescence-decay time  $\tau$  vs. the observation wavelength  $\lambda_{\text{obs}}$  for the ions  $\text{Yb}^{3+}$  in Ba-Nd-La metaphosphate glass ( $\Delta$ —0.2 wt.%  $\text{Yb}^{3+}$ ;  $\circ$ —5 wt.%  $\text{Yb}^{3+}$ ;  $\square$ —7 wt.%  $\text{Yb}^{3+}$ ), and the short-wave part of the luminescence spectrum of the  $\text{Yb}^{3+}$  ions at a concentration 0.2 wt.% (solid line).

wt.%). We investigated the transitions  $4F_{3/2} \rightarrow 4I_{9/2}$ ; and  $4F_{3/2} \rightarrow 4I_{11/2}$  of the  $\text{Nd}^{3+}$  ions,  $5D_{\sigma} \rightarrow 7F_0$  of the  $\text{Eu}^{3+}$  ions,  $2F_{5/2} \rightarrow 2F_{7/2}$  of the  $\text{Yb}^{3+}$  ions, and  $4F_{5/2} \rightarrow 6H_{5/2}$  of the  $\text{Sm}^{3+}$  ions. The measurements were performed at 4.2 K with a spectral resolution 1–4 Å.

In all the investigated cases, at large REI concentrations ( $> 1\text{--}3$  wt.%) we observed an appreciable decrease in the characteristic luminescence decay times  $\tau$  with decreasing  $\lambda_{\text{obs}}$  on the short-wave wing of the IBL (Fig. 1). At the same time, the decay kinetics change from almost exponential at wavelengths close to the maximum of the IBL to sharply non-exponential at  $E - E_0 > (1\text{--}1.5)\Delta$ , where  $E_0$  and  $E$  are the energies corresponding to the maximum of IBL and  $\lambda_{\text{obs}}$ , and  $\Delta$  is the half-width of the IBL (Fig. 2). For transitions whose Stark structure was well resolved (for example,

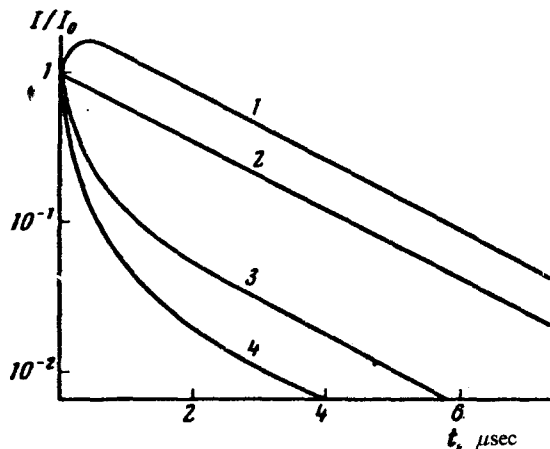


FIG. 2. Kinetics of luminescence decay of  $\text{Yb}^{3+}$  ions in  $\text{Na}_3\text{Nd}_{(1-x)}\text{Yb}_x(\text{MoO}_4)_4$ ,  $\lambda_{\text{obs}} = 9780$  Å (1); 9750 Å (2); 9728 Å (3); 9724 Å (4).

$\text{Nd}^{3+}$  in glasses), no flareup was observed, and the decay kinetics was close to exponential and depended little on  $\lambda_{\text{obs}}$  at  $\lambda_{\text{obs}} > \lambda_0$ , where  $\lambda_0$  is the wavelength corresponding to the maximum of the IBL of the transition between the lower Stark components. The effect increased with increasing concentration of the REI, and at low concentrations (0.1–0.3 wt.%) or (and) increased temperatures ( $kT \gg \Delta$ ) it did not appear at all.

The luminescence spectra, obtained with variable delay up to  $4\tau_0$  between the registered signal and the exciting pulse, have shown that the effect is accompanied by deformation of the luminescence contour and by a temporal shift of the short-wave edge of the contour towards larger  $\lambda$ .

The totality of the foregoing attributes allows us to conclude unambiguously that the observed effect is a spectral manifestation of nonresonant nonradiative transport of the excitation energy over the IBL contour, with production of a phonon. The transport mechanism is apparently the same for different REI and for matrices with greatly differing chemical compositions and structures.<sup>11</sup>

The probability of the elementary active transfer of excitation energy between two impurity centers (IC) separated by distance  $R$  and having a transition-energy difference  $\epsilon$ , can be represented in the case of incoherent interaction in the form  $W = C(\epsilon)/R^m$ , ( $m \geq 4$ ).<sup>11</sup> A calculation within the framework of the model of spectral packets<sup>17</sup> shows that under conditions when  $\delta \ll \Delta$ , and  $kT \ll \Delta$ ,  $N[\tau_0 C(\Delta)]^{3/m-1} \gg 1$  and in the case of pulsed excitation the luminescence intensity of the selectively excited IC with transition energy  $E$  can be described by the expression

$$I(E, t) = I(E, 0) \exp \left[ -t/\tau_0 - F(E)(t/\tau_0)^{3/m} \right], \quad (1)$$

where

$$F(E) = 4/3 \pi \tau_0^{3/m} \Gamma(1 - 3/m) N \int_0^E g(E - \epsilon) [C(\epsilon)]^{3/m} d\epsilon \quad (2)$$

$\delta$  is the homogeneous line width,  $N$  is the IC concentration,  $\tau_0$  is the time of the intracenter luminescence decay of an IC with energy  $E$ ,  $\Gamma(X)$  is the gamma function, and  $g(E)$  is the normalized IC distribution function with respect to the transition energies.

In the case  $E - E_0 \gg \Delta$ , expressions (1) and (2) are valid also in the case of broadband excitation, and (2) takes the simpler form

$$F(E) \cong 4.07 N \Gamma(1 - 3/m) [\tau_0 C(E - E_0)]^{3/m}. \quad (3)$$

Computer calculations in which  $g(E)$  was assumed to have a Gaussian contour have shown that (3) is valid within several percent already at  $E - E_0 > 0.8\Delta$ . Thus, it becomes possible to calculate the interaction parameters  $m$  and  $C(\epsilon)$  from the observed luminescence decay curves.

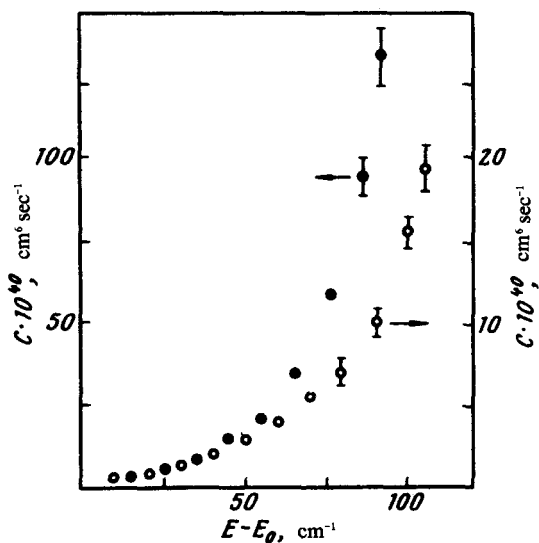


FIG. 3. Plots of  $C$  against  $(E - E_0)$  for the ions  $\text{Nd}^{3+}$  (●) and  $\text{Yb}^{3+}$  (○) in Ba-La metaphosphate glass.

These parameters were determined for the REI  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$  in phosphate glass by approximating the experimental decay curves by curves calculated by computer from formulas (1) and (3) at different values of  $m$  and  $C$ . The multipolarity of the interaction for both cases turned out to be close to  $m=6$ , corresponding to dipole-dipole interaction of the IC. Plots of the probability of the elementary transfer act against the difference between the transition energies of the interacting ions, determined by the parameter  $C(E - E_0)$  are shown in Fig. 3. Relations of this kind have apparently been obtained here experimentally for the first time. Data for other REI in different matrices, together with a discussion of the interaction mechanism, will be published later.

We note in conclusion that the proposed method of selective observation of the kinetics of luminescence of the short-wave wing of an IBL can be used to investigate nonresonant energy transfer between arbitrary IC with inhomogeneously broadened luminescence line, and the capabilities of the method can be additionally expanded by combining it with the method of selective laser excitation.<sup>[8]</sup>

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<sup>1)</sup> It is of interest to note variations of  $\tau$  within the limits of IBL of similar character were observed in<sup>[6]</sup> in polyphosphoric acids at 77 K.

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