Kinetics of the delocalization of excitations in disordered systems

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The kinetics of the delocalization of excitations [the autocorrelation function $P_{00}(t)$] in a disordered system of like centers has been determined experimentally down to a level of 10^{-3} for the first time. Only at this stage of the process is the diffusive asymptotic behavior approached. The experimental results agree with a theoretical prediction.

The nature of the long-range asymptotic behavior of the kinetics of the decay of primary excitations, on the one hand, and the time required to reach this asymptotic behavior, on the other, are topics of fundamental importance in the theory of the migration of excitations in disordered systems of like centers (donors). As yet we do not have an unambiguous theoretical solution of this problem. Three attempts have been made at experiments in this direction. In studies of the kinetics of the depolarization of β-active nuclei[1] and of the depolarization of the luminescence of a dye,[2] the decay has been followed over an order of magnitude, but this is not far enough for the onset of the asymptotic behavior. In the experiments of Ref. 3, on Yb^{3+} ions in a phosphate glass by time-varying selective spectroscopy, the behavior $P_{00}(t)$ was studied over a range down to 3×10^{-2}. In the interval 0.05–0.03 a behavior $P_{00}\sim t^{-3/2}$ was observed, and it was concluded from this behavior that the diffusive stage of delocalization had been observed. However, the narrow decay range that was studied and the presence of several factors which complicate a comparison with the theory (the pronounced dispersion of the radiative decay probabilities, the broadening over time of the luminescence band of the selectively excited centers, etc.) have motivated further research in this direction.

The migration of excitations through a system of donors distributed at random among the sites of a regular lattice is usually described by the equation

$$\dot{\tilde{P}}_{xy} = -\sum_z (n_z \nu_{zx} n_x \tilde{P}_{xy} - n_x \nu_{xz} n_z \tilde{P}_{zy}), \quad \tilde{P}_{xy}(t=0) = n_x \delta_{xy} c^{-1}. \tag{1}$$

Here $\tilde{P}_{xy}(t)$ is the conditional probability for the observation of an excitation at site x if this excitation was at y at the time $t=0$; $n_x=1$ (or 0) if site x is occupied (or not occupied) by a donor; $\langle n_x\rangle = c$; and $\nu_{zx} = \nu_0 r_0^6/|x-z|^6 = C_{DD}|x-z|^{-6}$ is the transition rate. The theoretical problem is one of calculating $P_{xy}(t) = \langle \tilde{P}_{xy}(t)\rangle$ (the average is over the occupation numbers n_q). In the present paper we study the autocorrelation function $P_{00} = P_{yy}$. We use the method proposed by Dzheparov[4] for calculating P_{00}. This method is based on a semiphenomenological system of equations, which can be written as follows in the Laplace representation ($f(\lambda) = \int_0^\infty dt e^{-\lambda t} f(t)$ and in the limit of low concentrations ($c\to0$, but $c^2 t$ is nonzero):

$$\lambda P_{xy} = \delta_{xy} - \sum_z (N^y_{zx} P_{xy} - N^y_{xz} P_{zy}), \tag{2}$$

$$N^y_{zx}(\lambda) = c\nu_{zx} Q(\lambda + \nu_{zx}) / Q(\lambda), \qquad z \neq y, \tag{3}$$

$$N^y_{yx} = N^y_{xy} c^{-1}, \quad Q(t) = \langle \exp(-\sum_z n_z \nu_{zx} t)\rangle = \exp(-\sqrt{\beta t}). \tag{4}$$

These equations correct the Scher-Lax semiphenomenological theory[5,6] of continuous random walks by incorporating the condition[7] $\lim_{x \to y} P_{x \neq y}(\beta t \gg 1) = cP_{00}(\beta t)$[7], the correct value of the first term in the series expansion of P_{xy} in c, and other exact limiting properties.[4,8] Joining the first two terms of the asymptotic behavior $P_{00}(\beta t \to \infty)$ of the solution of Eqs. (2)–(4) and the asymptotic behavior at moderate times ($\beta t \lesssim 1$) in accordance with Ref. 4, we find

$$P_{00}(t) = Q(t) + (1 - Q(t))[1 + \varphi(\mu\beta(t+\tau))^{-1/2}](\mu\beta(t+\tau))^{-3/2}, \tag{5}$$

where $\beta = (16/9)\pi^3 C_{DD} N_D^2$, N_D is the density of donors, $\varphi = 1.93$, $\mu = 0.79$, and $\mu\beta\tau = 3.62$. A distinctive feature of this expression is its diffusive nature ($P_{00}(t \to \infty) \sim t^{-3/2}$); another is the presence in the region $0.5 \leqslant \log \beta t \leqslant 2$ of a "reoscillation" in the coordinates [$\log P_{00}(t)$, $\log \beta t$] preceding the onset of the asymptotic behavior. In the original version of the theory of continuous random walks,[5,6] the kernels N^y_{zx} are given by (3) at all z, so that in the limit of small values of c we have $P_{00}(t) = Q(t) = \exp(-\sqrt{\beta t})$. A similar "exponential" asymptotic behavior of P_{00} follows directly from several other studies also (e.g., Refs. 9–11).

In the present experiments we use a method of selective excitation and detection of the decay kinetics of the luminescence of certain groups of Yb^{3+} centers in an inhomogeneously broadened resonant band associated with the $^2F_{5/2}(1)$–$^2F_{7/2}(1)$ transition. In selecting the particular system and the experimental conditions we were attempting to maximize the correspondence with the theory. The most convenient system turned out to be the optically isotropic crystal $La_{0.96}Yb_{0.04}P_5O_{14}$ with a half-width $\Delta = 3.8$ (1) cm^{-1} for the inhomogeneously broadened band, with $E_{max} = 10\,251$ cm^{-1}, and with a radiative decay time $\tau_0 = 1400$ (20) μs. At this value of Δ it was simple to achieve a selectivity in terms of excitation pathway (a laser using a $LiF:F_2^+$ crystal with an output-band half-width $\leqslant 0.5$ cm^{-1}) and also in terms of detection pathway (a DFS-12 double monochromator with a spectral slit $\leqslant 0.8$ cm^{-1} wide). Here Δ was small in comparison with the Stark splitting of the $^2F_{7/2}$ and $^2F_{5/2}$ levels (ΔE_{12}, $\Delta E_{1'2'} > 150$ cm^{-1}), so that by adjusting the sample temperature [$T = 27.0$ (5) K] we were able to arrange the condition $\Delta \ll kT \ll \Delta E_{12}$, $\Delta E_{1'2'}$, which is equivalent to producing a system with two levels and with an energy transfer which is symmetric in terms of the spectrum of the inhomogeneously broadened band. A study of the time-resolved luminescence spectra confirmed that ν_{xz} does not depend on the energy deviation within the inhomogeneously broadened band. This conclusion follows from the absence of any significant deformation of the broad secondary-luminescence band for various excitation frequencies E_{ex} and from the similarity of this spectrum to that during wide-band excitation (Fig. 1). The absence of any significant disperison in the values of τ_0 over the inhomogeneously broadened band and the

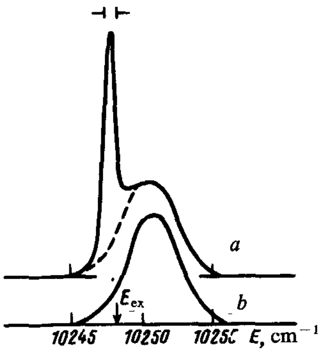

FIG. 1. Luminescence spectra of Yb^{3+} ions. *a*—Selective excitation, $E_{ex} = 10\,248$ cm^{-1}, $t_{del} = 0.4$ ms; *b*—wide-band excitation.

constancy of the half-width of the narrow peak of the primary luminescence (Fig. 1) over time are also important differences between this particular system and a phosphate glass.[3]

The kinetic measurements are carried out on a high-precision apparatus[12] by a method of multichannel photon counting, with a 1024-channel analyzer (the scanning rate is 10 μs/channel). Figure 2 shows the kinetics corresponding to the narrow luminescence peak $I(t)$ at the excitation frequency, $E_{ex} = 10\,248$ cm^{-1} (curve 1), and to the broad band of secondary luminescence, $I_b(t)$, $E_b = 10\,253$ cm^{-1} (curve 2). The value

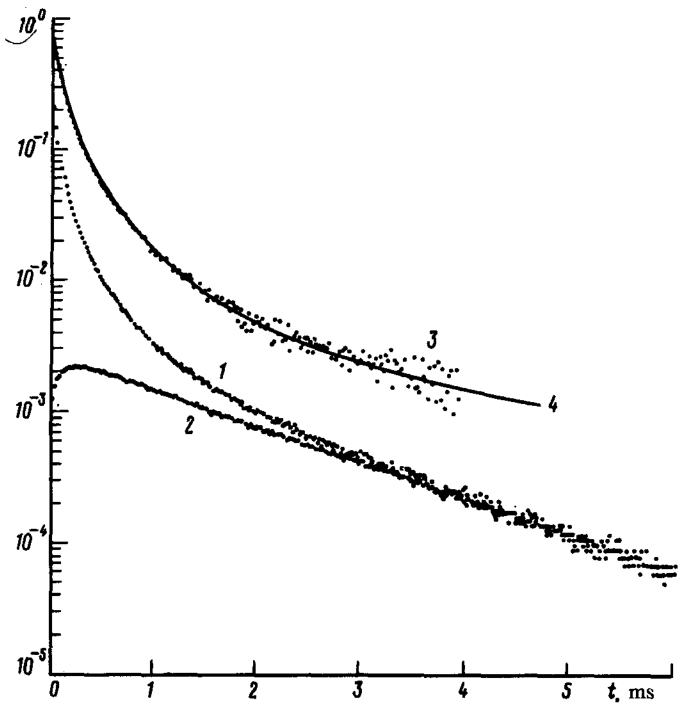

FIG. 2. Luminescence kinetics of Yb^{3+} ions from measurements at the frequencies E_{ex} (1) and E_b (2); experimental curve (3) and theoretical (4, with $\beta = 27$ cm^{-1}) curve of the function $P_{00}(t)$.

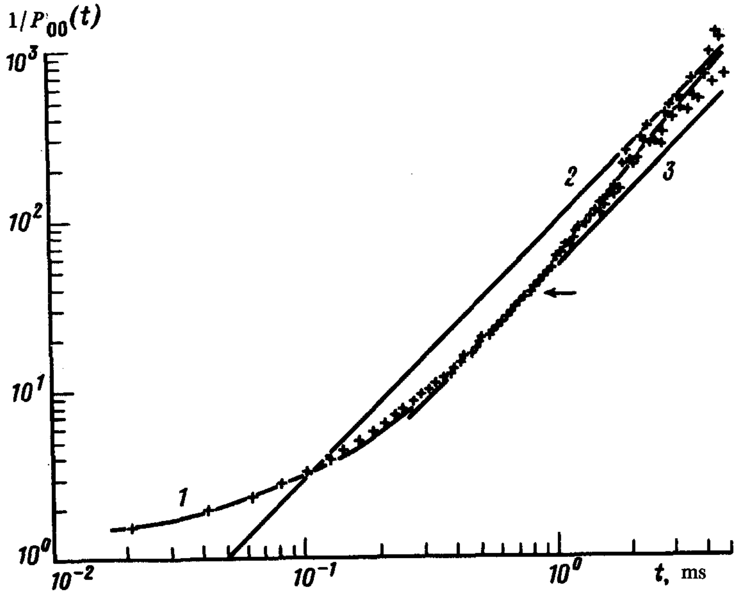

FIG. 3. Experimental (+) and theoretical (1) curves of $P_{00}(t)$ in terms of the coordinates $\log P_{00}(t)$ and $\log t$; 2—diffusive asymptote; 3—"false" diffusive asymptote.

of E_{ex} was found empirically in careful experiments carried out to maximize the change in the autocorrelation function $P_{00}(t) = (I(t) - \alpha I_b(t))/I_0(t)$, where $I_0(t)$ is the radiative-decay function of the Yb^{3+} ions, and the factor α normalizes the function $I_b(t)$ to the values of the function $I(t)$ in the remote stage of the decay, i.e., at $P_{00}I_0 \ll I_b\alpha$. From curve 3 in Fig. 2 we see that the range of $P_{00}(t)$ achieved amounts to three orders of magnitude. Analysis of the early stage of the decay by the method of Ref. 3 shows that the dipole-dipole interaction of Yb^{3+} ions dominates the transfer of excitations between these ions, and it allows us to determine the constant of the transfer, $\beta = 30 \pm 3$ ms^{-1}. This value is essentially the same as the value $\beta = 27 \pm 1$ ms^{-1} which results in the best fit of curve 3 by Eq. (5). Figure 3 shows the function $P_{00}(t)$ as a plot of $-\log P_{00}$ versus $\log t$. In the region $0.5 \leqslant \log P_{00} \leqslant 2$, there is clearly a "reoscillation," in complete accordance with the theoretical prediction (curve 1).

It can be concluded from these results that these experiments have yielded the first observation of the onset of the diffusive asymptotic behavior in the kinetics of the delocalization of excitations in a disordered system of donors. These results confirm the theoretical prediction that this onset of asymptotic behavior in the limit of small values of c should occur at $\log \beta t \geqslant 2$ in the third order of the kinetics of the decay of the primary excitations. Expression (5) turns out to be quite accurate and can be recommended for use in analyzing experimental data.

In addition, these results do not support the earlier conclusion[3] that a diffusive stage of the kinetics of delocalization was observed at $P_{00} \sim 0.05$–0.03. The arrow in Fig. 3 shows the final point of the interval studied in Ref. 3. Clearly, although we see $P_{00} \sim t^{-3/2}$ here, the kinetics of the delocalization is still far from the asymptotic diffusive behavior.

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