

Diffusive delocalization of electronic excitations through a disordered system of centers

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A diffusive step has been detected experimentally for the first time in the egress of excitations from a source node as a result of migration through a disordered system of centers. The time at which the diffusive step sets in and the kinetics of this step have been determined. The coefficient of disordered diffusion has been measured. Its irrational concentration dependence has been determined.

One of the most effective methods for studying the incoherent transport of electronic excitations in a solid is the method of time-dependent selective spectroscopy.^{1,2} This method can be used to directly study the spatial migration of excitations in a collection of like particles having a spread of transition frequencies. By selectively exciting centers with a fixed transition frequency by a short laser pulse under special conditions, such that the excitation frequency changes upon a spatial replacement of the center, we are able to directly observe the kinetics of the emptying of the originally excited centers by measuring their luminescence intensity.

The egress (migration) of excitations in disordered systems was originally assumed to be irreversible, and its kinetics was described by the Forster expression³

$$I(t) = \exp(-gt)^{3/S}, \quad (1)$$

where g is the average rate of the irreversible transport, and S is the multipolarity of the interaction. Huber *et al.*⁴ found a simple way to allow for the return of excitations to the initial center, at least from the center nearest the initial center. For $I(t)$ they derived the same functional relationship [see expression (1)], with the rate g replaced by $g_0 = g \cdot 2^{(1-S/3)}$. Here the average velocity of the reversible migration g_0 , is related to the microefficiency of the interaction, C_{dd} , and to the particle density n by

$$g_0 = \left[\frac{4\pi}{3} n \Gamma\left(1 - \frac{3}{S}\right) \right]^{S/3} C_{dd} 2^{(1-S/3)}. \quad (2)$$

After a long time, the binary model for incorporating reversibility breaks down,⁴ since we need to consider returns to the initial center from more remote migration trajectories. It is logical to assume that this process consists of a diffusion similar to a diffusion through an ordered system of centers, but it is a very complicated matter to carry out exact calculations of this process in a disordered system. This migration process has been the subject of many theoretical papers,^{5–10} most of which have derived diffusive solutions for the long-term asymptotic behavior. All of these solutions, however, have been based on assumptions whose validity is difficult to analyze. It is

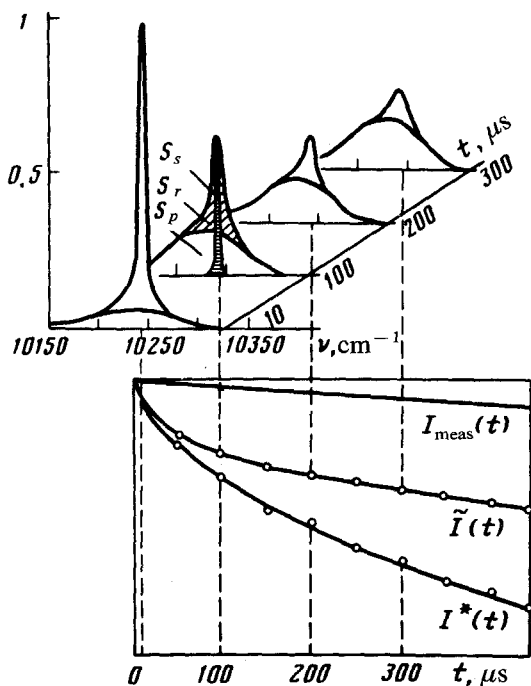


FIG. 1. Spectral-temporal dynamics of the migration of the energy of excitations through the nonuniform, broadened ${}^2F_{7/2}(1) \rightarrow {}^2F_{5/2}(1)$ band of Yb^{3+} ions.

thus important to experimentally test for the presence or absence of a diffusive step in the decay kinetics¹⁾ of the initial centers at large times t .

In the present experiments we studied a spectrally and spatially disordered medium: a barium-aluminum phosphate glass activated with Yb^{3+} ions in concentrations $n_1 = 1.1 \times 10^{20} \text{ cm}^{-3}$ and $n_2 = 2.9 \times 10^{20} \text{ cm}^{-3}$. For the selective laser excitation we used a nanosecond-pulse laser with an active medium consisting of a LiF crystal with color centers. The temperature of the samples, $T = 80 \text{ K}$, was chosen to allow a frequency-independent reversible migration mechanism, in accordance with the theoretical models. The emission spectrum of the spectrally inhomogeneous set of interacting centers resolves into two components in this case (Fig. 1): a narrow resonant peak corresponding to the emission of the initially excited centers (the area under this peak is S_s ; this is the area with oblique hatching in Fig. 1) and a wide, inhomogeneously broadened pedestal (of area S_p), which corresponds to the emission of other centers involved in the migration. To determine the egress kinetics $I(t)$ we measured the luminescence decay $\tilde{I}(t)$ in selective measurements at the frequency of the selective excitation. The passband of the spectrometer in these measurements is shown by the horizontal hatching in Fig. 1a, whose area is S_r . As can be seen from Fig. 1, we cannot obtain information on $I(t)$ directly from the experiment, since the pedestal contributes significantly to $\tilde{I}(t)$. To eliminate this pedestal contribution, we corrected the kinetics of the $\tilde{I}(t)$ decay each $50 \mu\text{s}$ by multiplying by a factor $K(t)/K(0)$ [$K(t) = S_r/S_s$], found from time-resolved spectra (Fig. 1): $I^*(t) = \tilde{I}(t)K(t)/K(0)$. The spontaneous-emis-

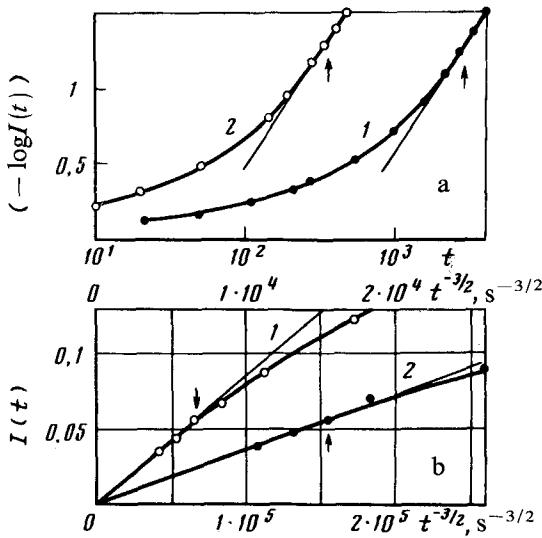


FIG. 2. Analysis of the time-dependent and diffusive steps in the kinetics of the egress of excitations from an initial center. ●— $n_1 = 1.1 \times 10^{20} \text{ cm}^{-3}$; ○— $n_2 = 2.9 \times 10^{20} \text{ cm}^{-3}$. a: Plot of $-\log I(t)$ versus $\log t$. b: $I(t)$ versus $t^{-3/2}$.

sion channel for the decay of the excitations was eliminated by dividing the decay function $I^*(t)$ by the radiative-decay function $I_{\text{rad}}(t)$, measured by the same method at $T = 4.2 \text{ K}$ for a sample with $n_3 = 2.9 \times 10^{19} \text{ cm}^{-3}$, in which the migration was weaker: $I(t) = I^*(t)/I_{\text{rad}}(t)$.

Let us analyze the time evolution of the population of the initial centers, $I(t)$. Putting the early stage of the kinetics in a linear form by plotting $-\log I(t)$ versus $t^{1/2}$ reveals that the time-dependent part of the kinetics ($t \leq t_b$) corresponds well to decay law (1) and is evidence of a dipole-dipole ($S = 6$) interaction of the Yb^{3+} ions. From the slope of the lines we find the average velocity of the reversible migration: $g_0(n_1) = 3 \times 10^3 \text{ s}^{-1}$ and $g_0(n_2) = 2.3 \times 10^4 \text{ s}^{-1}$. From these values and (2) we can calculate the microefficiency of the Yb^{3+} - Yb^{3+} interaction: $C_{dd} = 10 \text{ nm}^6/\text{ms}$.

Plotting the kinetics as $-\log I(t)$ versus $\log t$ (Fig. 2b) reveals a deviation from law (1) at $t > t_b$: a replacement of the power-law function $0.434g_0^{3/2} \times 10^{0.5 \log t}$ by the linear function $3/2 (\log W_{\text{diff}} + \log t)$, which corresponds to a diffusive egress kinetics, $I(t) = (W_{\text{diff}} t)^{-3/2}$. Equating the derivatives of these two functions, we find the time marking the boundary between them to be $t_b = (S/2)^{2/3} g_0^{-1}$. Using $S = 6$, we then find $t_b = 9g_0^{-1}$, as shown by the arrows in the figures. The observation of a decay law with a slope of $3/2$ in these coordinates is the first experimental evidence for the existence of a diffusive step in the migration of excitations through a disordered system of centers. This result is confirmed by the fact that a plot of the decay kinetics $I(t)$ in the coordinate $t^{-3/2}$ reveals a straight line and by the fact that this straight line passes through the origin (Fig. 2). The slope of the linear part of this function in the limit $t^{-3/2} \rightarrow 0$, which corresponds to the diffusive step in the egress kinetics in the limit $t \rightarrow \infty$, gives us diffusive-migration velocities $W_{\text{diff}}(n_1) = 2.5 \times 10^3 \text{ s}^{-1}$ and $W_{\text{diff}}(n_2)$

$= 2 \times 10^4 \text{ s}^{-1}$, in approximate agreement with $g_0(n_1)$ and $g_0(n_2)$.

A calculation of the diffusion coefficients D_{dis} from the expression $W_{\text{dif}} = 4\pi n^{2/3} D_{\text{dis}}$ for these densities n_1 and n_2 yields $0.9 \times 10^{-11} \text{ cm}^2/\text{s}$ and $3.6 \times 10^{-11} \text{ cm}^2/\text{s}$. The ratio of these values, 4, is approximately equal to the value $(n_2/n_1)^{4/3} = 3.64$, confirming that the diffusion coefficient is an irrational function of the concentration of centers: $D_{\text{dis}} \sim n^{4/3}$.

¹¹The theoretical and experimental foundations of this formulation of the problem and the first versions of its solution are discussed in detail in Ref. 11.

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