EXCITON TRANSPORT IN NAPHTHALENE ALLOYS: A TRANSITION FROM PERCOLATION TO DIFFUSION +

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Received 9 August 1982

Steady-state singlet excitation transport in ternary naphthalene crystals ($C_{10}H_8/C_{10}D_8/\beta$-methylnaphthalene) fits diffusion models at 4.2 K, but not at 1.8 K, where it fits a percolation model.

Simple diffusion models have repeatedly been suggested for the "critical" electronic energy transport in substitutionally disordered binary crystals [1–3]. Our old naphthalene steady-state singlet data [4], have been fitted to such models with apparent success [2,3]. We have recently pointed out [5] that our low-temperature time-evolution studies do not fit homogeneous diffusion models, but do fit heterogeneous cluster kinetics. We show here that our new steady-state data can be fitted by diffusion models at 4.2 K but not at 1.8 K. This agrees with our recent theoretical studies on the quantum-mechanical basis for the clusterization of exciton states and the resulting percolative transport [6–8].

Experimentally, the sample composition was much better controlled than in previous work [4,9]. Also the evaluation of the relative intensities of the supertrap and the guest fluorescence was much refined, especially concerning the phonon side-band contributions (see fig. 1). Details, as well as a complete description of the experimental procedures, are given elsewhere [10]. The experimentally determined observable

$$P = I_S/(I_S + 2I_g),$$

where I_S is supertrap emission and I_g guest emission, is plotted against the guest concentration (fig. 2), normalized with respect to the critical concentration $C_{1/2}$ (the value of the latter is 0.75 mol fraction for 1.8 K and 0.63 for 4.2 K).

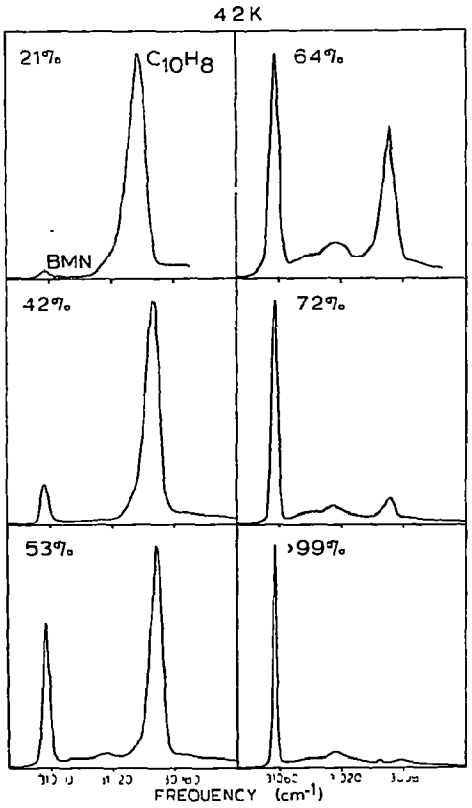

Fig. 1. Guest and supertrap fluorescence spectra for the ternary crystal system $C_{10}D_8/C_{10}H_8$/BMN. The guest concentration was varied while maintaining a constant supertrap·guest concentration ratio of 10^{-3}. This set of spectra was recorded at a temperature of 4.2 K. The BMN 0–0 zero-phonon peak is located at 31061 cm^{-1} for a 100% $C_{10}H_8$/BMN crystal.

+ Supported by NSF Grant DMR 8000679.

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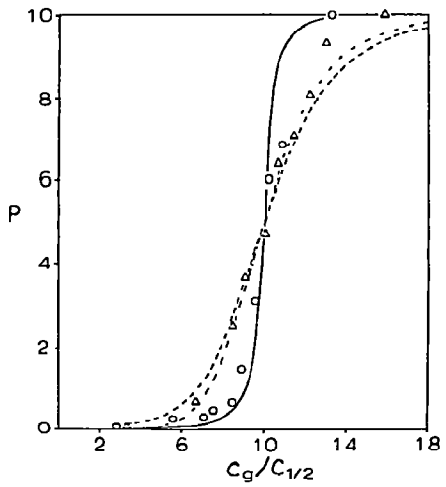

Fig 2 Trapping probability versus reduced concentration $C_{1/2}$ is defined as the concentration corresponding to $P = 0.5$. Experimental circles are 1.8 K data, triangles are 4.2 K data. Theoretical: the solid and dashed lines correspond to percolation and the Loring and Fayer calculation respectively, the dot–dashed line was calculated using the Blumen and Silbey model. The Blumen and Silbey and the Loring and Fayer curves assume octupole–octupole transfer within a two-dimensional continuum. The experimental data and the percolation and Blumen and Silbey curves are all with $C_s/C_g = 0.001$. The Loring and Fayer curve kept C_s constant at $C_s = 0.001$. Changing the Loring and Fayer curve to account for a constant C_s/C_g ratio would only add a small correction. As a comparison, if the Blumen and Silbey equations were calculated using $C_s = 0.001$ then the result would lie half way between the dot–dashed and the dashed lines for $C_g/C_{1/2} < 1.0$, for $C_g/C_{1/2} > 1.0$ the result is essentially identical to the Loring and Fayer curves.

Fig. 2, in addition, compares the experimental P (for $C_s/C_g = 10^{-3}$) with the diffusion and percolation models. The percolation results were based on Monte Carlo simulations [11] on a 400 × 400 square lattice with NN interactions and a constant $C_s/C_g = 10^{-3}$. The Loring and Fayer and the Blumen and Silbey curves are based on octupole–octupole transfer in a two-dimensional continuum. The Blumen and Silbey curve is for $C_s/C_g = 10^{-3}$. The Loring and Fayer result is based on $C_s = 10^{-3}$ and with the adjustable parameter set at $R_0 = 8$ Å. The Blumen and Silbey result for $C_s = 10^{-3}$, however, would be identical to that of Loring and Fayer for $C_g > C_{1/2}$, and twice as close as shown in fig. 2 to the Loring and Fayer curve for $C_g < C_{1/2}$. The upshot from this is that the two diffusion models give identical results, within our experimental uncertainties. However, the difference between the diffusion and percolation model is significant, especially in the vicinity of the critical threshold.

The diffusion models obviously ignore the clusterization of guest sites and the concomitant energy mismatches (of cluster states), as they assume the high temperature limit for guest–guest transfer. At low temperature, however, forward and backward transfers can be very different, especially for longer-range "hops". In addition, the random hopping idea (based on localized states) is more suspect at lower temperatures. Even at 4.2 K, where the diffusion model does fit the data, it should not be taken too literally. The fitting parameter ($R_0 = 8$ Å), with a NN distance of 5.1 Å and a lifetime of 120 ns, gives a nearest-neighbor transfer time of 200 ps, while the usual estimate [12] is ≈1 ps. The slow transfer rate may be a manifestation of an effective averaging over slow back-transfer between energy-mismatched clusters, etc.

The fit to the percolation model excludes the supertransfer case [11] and has to be based on models where transport inside the supercluster is not infinitely fast but rather inefficient due to the ramified topology. This has been shown before [11,13] both experimentally and via simulations, where the simulations included a quasi-coherent ("correlated walk") description of the exciton motion inside the disordered guest lattice. A rough fit would be achieved with a correlation value [13] of $l \gtrsim 10$, i.e. one scattering event per ten or more transfers.

In summary, our more refined experimental data allow us to critically test current models of energy transfer in disordered media. The generalized diffusion models of GAF [3] and of Blumen and Silbey do fit the 4.2 K data, even though the resulting interaction parameter may be physically unrealistic. They do *not* fit the 1.8 K data. The better fit of the percolation model at 1.8 K is reasonable on two physical counts. The longer-range transfers are very inefficient at 1.8 K in view of the cluster energy mismatches, and can thus be effectively ignored or "cut-off". The shortest-range transfers at 1.8 K are quasi-coherent, resulting in a sharp rise in transport efficiency as the nearest-neighbor infinite cluster topology changes from effectively one-dimensional ("ramified") to two-dimensional.

We thank R.F. Loring and M D Fayer for a preprint of their work and several private communications We would also like to thank A. Blumen and R. Parson for fruitful discussions.

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