

UNIVERSALITY AND CRITICAL EXPONENTS OF ENERGY TRANSPORT IN BINARY CRYSTALS: ³B_{2u} NAPHTHALENE *

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Exciton migration experiments on isotopically mixed naphthalene crystals reveal a universal behavior with *reduced* donor concentration, irrespective of temperature, acceptor species or acceptor concentration, giving a *very wide scaling region*, with critical exponents $\gamma = 2.1 \pm 0.22$ and $\beta = 0.13 \pm 0.05$, consistent with two-dimensional dynamic exciton percolation.

“Critical” concentrations of excitation transferring donor species found in insulators and semiconductors have been of much recent interest and debate [1–5]. The concept of an Anderson–Mott mobility edge in ruby and inorganic glasses [4–6] has been juxtaposed [1] with kinetic models based on diffusion and percolation [7,8]. Isotopically mixed organic crystals offer a number of advantages for the study of substitutionally disordered systems. Complete miscibility of donor and “host” species, controlled and uncorrelated donor and acceptor concentrations, excellent crystal quality at all concentrations, no radiative trapping or phonon bottleneck, easy spectral (300 cm⁻¹) and temporal resolution ($\tau = 2.5$ s) and well documented excitation exchange interactions [9].

While the scaling and critical exponents of transport properties have been of much interest [10], excitation transport has been treated in terms of a particularly simple picture, which is analogous to two- and three-dimensional magnetic transitions [11], involving the same critical exponents (β, γ, δ), and suggesting a straightforward test case for a “percolation transition” [10]. We present here a preview of a systematic experimental investigation of critical energy

transport [12] in the well characterized naphthalene system [13]. *It reveals “universality” and an extremely wide scaling region, resulting in non-classical critical exponents that are valid over a very wide range of the order parameter, in excellent quantitative agreement with percolation theory results.*

Highly purified, potassium fused and zone refined naphthalene C₁₀H₈ and C₁₀D₈ were used to prepare the samples of series B and C, through successive dilution of a “C₁₀H₈/BMN standard” with C₁₀D₈, giving a constant betamethylnaphthalene (BMN) mole fraction *S* (with respect to C₁₀H₈) throughout series B, and another constant *S* value for series C. The series A data utilize a “naturally” occurring impurity in the C₁₀H₈ sample (not potassium fused), which creates both C₁₀D₈ and C₁₀H₈ X-traps. Thus our experimental system consists of C₁₀D₈ *host* molecules, C₁₀H₈ donor (guest, trap) molecules and BMN (in series B and C) or C₁₀H₈ X-trap (in series A) *acceptor* molecules (supertrap, sensor). The relative intensities of the steady-state donor and acceptor phosphorescence are measured and expressed in terms of acceptor emission photon-count (*I_S*) and total acceptor and donor emission photon-count (*I_{total}*). As at least 99.9% of the acceptor excitations are derived by supertrapping from the donor, we equate the ratio *I_S*/*I_{total}* with *P(C, S, T)*, the probability of a donor exciton being supertrapped by an acceptor, within

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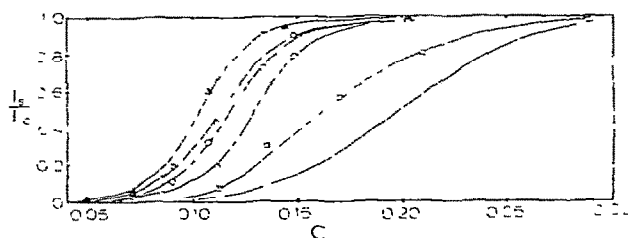


Fig. 1. Donor concentration dependence of the energy transport measure $I_S/I_{tot} = I_S/(I_S + I_d)$, where I_S is the acceptor ("supertrap") phosphorescence (0-0) and I_d is that of donor $C_{10}H_8$ for series A (X-trap $S \approx 10^{-4}$, diamonds 1.7 K, hexagons 4.2 K), series B (BMN, $S = 10^{-3}$, circles 1.7 K, triangles 4.2 K) and series C (BMN, $S = 10^{-4}$, crosses 1.7 K, squares 4.2 K). The lines are visual guides.

its lifetime τ_0 , in a sample with donor (guest) mole fraction C , temperature T and acceptor/donor concentration ratio S .

The results over a wide range of donor concentrations are given for the three series of samples (with different acceptor species or acceptor concentration) at two temperatures (fig. 1). We see obvious effects on the critical concentration C_c and its steepness, the former moving to lower C while the latter becomes more abrupt with increases in either temperature or acceptor concentration (for a given acceptor species). This is certainly *not the expected behavior for an Anderson-Mott mobility edge*, which should be effectively independent of S (at such low absolute acceptor concentrations of 10^{-4} to 10^{-6}) and should rather "erode" with increasing temperature [14,15]. Fig. 2 shows the same curves as fig. 1, this time plotted against the *reduced* concentration C/C_c . The striking feature is obviously the *universality* of the curve, compared to the six curves of fig. 1.

The cluster model of exciton "percolation" [11, 16] is based on the mathematical functions \bar{P}_∞ (cluster percolation probability) and I_{av} (average finite cluster size). These functions have the critical exponents β and γ associated with them [10,11].

$$\bar{P}_\infty \propto |C/C_c - 1|^\beta, \quad I_{av} \propto |C/C_c - 1|^{-\gamma}, \quad (1)$$

where C is the donor concentration, C_c is the critical concentration, and C/C_c is the *reduced concentration*. The results of the exciton percolation model (with a sharp cut-off of interactions for sites more than n "lattice units" away) have a simple form in the fol-

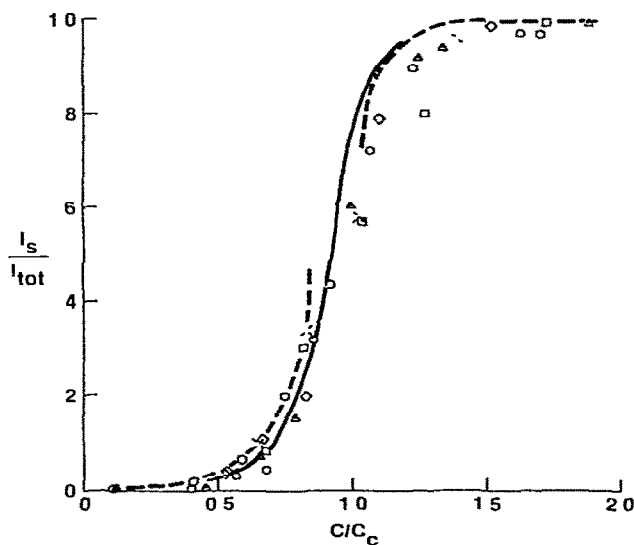


Fig. 2. Universal energy transport curve. The data points and designations are the same as in fig. 1. For each family of data points (given S, T) C_c was derived from fig. 1 via eq. (3), using $P = I_S/I_{tot}$. The dashed lines are the theoretical results, based on eqs. (2) and (4') (with a proportionality constant of 5×10^{-3} and \bar{P}_∞ and I_{av} values from ref. [18]). The solid line is a more exact percolation function (ref. [11]) which is applicable through the complete concentration range.

lowing concentration domains [11,12]

$$P = \bar{P}_\infty, \quad C \gg C_c, \quad S \ll 1, \quad (2)$$

$$P = S^{1/\delta}, \quad C = C_c, \quad S \ll 1; \quad (3)$$

$$P \propto I_{av}, \quad C \ll C_c, \quad S \ll 1, \quad (4)$$

where $P(C, n, S)$ is the probability of the donor exciton being trapped by the acceptor, whose effective relative concentration (with respect to donor) is S , and $\delta = \gamma/\beta + 1$. The above model holds whether the intracluster exciton transfer is "coherent" or "incoherent", instantaneous or time dependent. However, in the latter case the connectivity (defined by n) is time dependent, resulting in "dynamic percolation" [16,17]. While $C_c, I_{av}, \bar{P}_\infty$ and thus eqs. (2)–(4) all depend on n (and in the dynamic model [12, 17], on time, temperature and S) this dependence can be removed by a transformation to reduced concentrations [11,18],

$$P(C/C_c) = \bar{P}_\infty(C/C_c), \quad C/C_c \gg 1, \quad (2')$$

$$P(C/C_c) = I_{av}(C/C_c), \quad C/C_c \ll 1. \quad (4')$$

As it has been demonstrated [18] that $\bar{P}_\infty(C/C_c)$ and $I_{av}(C/C_c)$ have little or no dependence on n , we expect the above relations to be *universal* (i.e., to show no dependence on acceptor concentration S , temperature, or lifetime [12]). While eq. (3) has an explicit S dependence, it is a very weak one ($\delta \approx 17$) [10,11].

In the dynamic percolation model [17], the value of C_c is strongly dependent on time, temperature, and S (acceptor concentration), even for very low S values. This is one major distinction relative to an Anderson-Mott mobility edge model [14]. Another feature of the percolation model is that eqs. (2') and (4') in combination with eq. (1), predict

$$P(C/C_c) \propto |C/C_c - 1|^\beta, \quad C/C_c \gg 1, \quad (5)$$

$$P(C/C_c) \propto |C/C_c - 1|^{-\gamma}, \quad C/C_c \ll 1. \quad (6)$$

Assuming a smooth behavior of P , the largest deviations from universality should be at the critical concentration C_c . In fig. 1 is plotted the experimental percolation probability, I_S/I_{tot} , versus donor concentration for the six experimental systems, each with constant S . While fig. 1 indeed shows the wide variation of C_c with temperature and effective acceptor concentration, plotting the data on a reduced concentration scale in fig. 2 demonstrates its universality. The merging of all six curves is achieved through eq. (3) with no adjustable parameter. Also plotted in fig. 2 are the limiting functions given by eqs. (2') and (4'). These asymptotic functions (dashed lines in fig. 2) and the experimental points are in excellent agreement, considering the combined experimental and simulation uncertainties. An even better test is the conventional log-log plot of the same quantities, as shown in fig. 3. Here the dashed lines, corresponding to the above asymptotic functions, give directly the exponents β and γ (for $C/C_c \gg 1$ and $C/C_c \ll 1$, respectively).

It is generally accepted that triplet exciton transfer in naphthalene is predominantly in the ab plane (with out-of-plane interactions at least a factor of 10^5 higher [19]). We thus expect critical exponents based on a two-dimensional topology. From fig. 3 we experimentally obtain values of $\beta = 0.13 \pm 0.05$

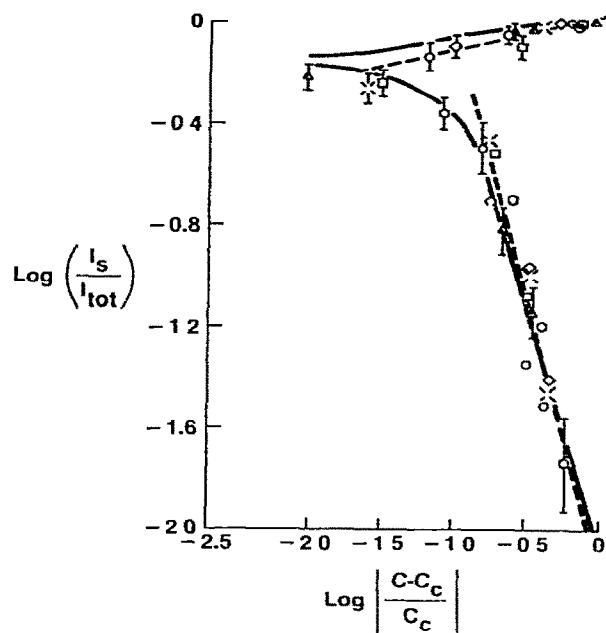


Fig. 3. "Scaled" energy transport curve. The data points and designations are the same as in figs. 1 and 2. Error bars were added to a few points to indicate experimental uncertainties. The dashed lines are least-squares fits to the experimental data, giving $\gamma = 2.1 \pm 0.2$ and $\beta = 0.13 \pm 0.05$. Alternatively, they can be viewed as theoretical straight lines whose slopes are defined by the above values of β and γ . The full line is a theoretical curve explained in ref. [12], using the same proportionality constant as in fig. 2

and $\gamma = 2.1 \pm 0.2$, in good agreement with mathematical values for the two-dimensional long-range percolation problem [11] of $\beta = 0.14$ and $\gamma = 2.1$.

We conclude that the critical-exponents test gives ample proof for the consistency of our experimental results with a cluster model of exciton percolation. The wide scaling region is particularly interesting and indicates that a "percolation transition" can occasionally be revealed by its characteristic behavior far away from the critical point. We know of no other model that would account for the striking patterns revealed by the long-lived triplet excitations in these isotopically mixed naphthalene crystals.

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